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(54) PROCESS OF FORMING POLYOLEFIN FIBRES

(71) We, CROWN ZELLERBACH CORPORATION, a Corporation organized and existing under the Laws of the State of Nevada, United States of America, of One Bush Street, San Francisco, California, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 The polymerization of olefins into polyolefins is well established in the art. Early processes employed in the high pressure procedure to produce the low density polyethylene. More recently, the use of coordination catalysts has permitted the polymerization of olefins to be effected at lower pressures to produce high density polyolefins.

The formation of fibers or filaments of polyolefins has previously been effected by extruding the polyolefin through spinnerets with the formation of continuous filament lengths, with subsequent chopping of such filaments into staple fibers.

Another approach has been to form so-called "fibrils". The formation of such fibrils is described in U.S. patents 2,999,788; 2,988,782 and 2,708,617.

All of these prior art processes teach the formation of the polymeric material first, with subsequent conversion into fibers. The first of the prior art processes mentioned involves the general steps of polymerizing the monomer to the polymer, precipitating the polymer as a crumb from the reaction medium, forming the precipitated polymer into pellets, heating the pellets and extruding them through spinnerets to form filaments, and chopping the filaments into staple. The second type of prior art process (fibrils) involves forming the polymer and redissolving the polymer to precipitate it in the form of fibrils. As is seen by the number of steps involved, such processes are relatively [Price 25p]

expensive in view of the large number of intermediate handling steps. In addition, there is a practical upper limit on the molecular weight of the polymer employed in such prior art processes because of viscosity limitations.

A process has recently been invented whereby polyolefin fibers may, surprisingly, be formed directly from olefin monomers during polymerization. This process is described in copending application No. 47373/69 (Serial No. 1,287,917). In the process described in the aforementioned application, olefins are polymerized in a suitable reaction medium in the presence of a coordination catalyst at a relatively high reaction rate and under conditions of relatively high shear stress to produce fibers directly which have a gross morphology and size similar to natural fibers. Such fibers will be referred to hereinafter as "nascent fibers". The nascent fibers thus manufactured are made up of "macrofibrils" which generally have a diameter greater than about 1 micron.

The present process forms polyolefin fibers of very high molecular weight by first forming a fibrous gel which does not contain discrete (free-floating) fibers, and then subjecting the gel to a relatively high shear stress whereby discrete fibers appear.

The process of the present invention comprises firstly forming a gel of high molecular weight linear polyolefin, said gel comprising a fibrillar structure of fibrous polyolefin defining a network of interconnecting capillary spaces filled with organic solvent, any shear stress applied in formation of the gel being insufficient to form discrete polyolefin fibers, and secondly subjecting the gel to a shear stress sufficient to form discrete polyolefin fibers.

Figure 1 is a schematic representation of one form of apparatus suitable for forming the fibrous gel of the process of the present invention.

Figure 2 is a schematic representation of

another form of apparatus suitable for forming the fibrous gel of the process of the present invention;

Figure 3 is a schematic view, partially in section, illustrating one form of commercial pulp refiner suitable for refining the fibrous gel of the present process into discrete fibers;

Figure 4 is a fragmentary plan view of a conventional refining plate section employed in the refiner of Figure 3 (the dotted lines in the view indicating the complete plate section);

Figure 5 is a graph depicting the yield of polyethylene fibers as a function of reaction time and temperature;

Figure 6 is a graph depicting the yield of polyethylene fibers as a function of reaction temperature;

Figure 7 is a graph depicting the minimum apparent specific reaction rate required to form fibrous gel as a function of the reaction medium and temperature;

Figure 8 is an electron microphotograph of microfibrils in the fibrous gel; and

Figure 9 is an electron microphotograph of the microfibril structure after refining.

In the present invention, a fibrous polyolefin gel is first formed and this gel is subsequently mechanically refined to produce very high molecular weight polyolefin fibers.

The fibrous gel may be formed by any one of three procedures. The fibrous gel may be directly formed by polymerizing an olefinic monomer in the presence of a coordination catalyst and in a solvent for the polymer, at a temperature below the melt dissolution temperature of the polyolefin to be formed. The reaction rate must, as discussed below, be sufficiently rapid to effect formation of the gel. Alternatively, the fibrous gel may be indirectly formed by first polymerizing in the presence of a coordination catalyst and in a solvent for the polymer the olefinic monomer, at a temperature above the melt dissolution temperature of the polyolefin to be formed, and then cooling the polyolefin solution thus obtained to a temperature below the melt dissolution temperature of the polyolefin to form a fibrous gel. The third alternative is to form the fibrous gel indirectly by forming a solution of a preformed, high molecular weight polyolefin at a temperature above the melt dissolution temperature of the polyolefin, and then cooling the polyolefin solution thus obtained to a temperature below the melt dissolution temperature of the polyolefin to form a fibrous gel. As discussed below, it is necessary to subject the solution to shear stress during cooling in the third embodiment and preferable to do so in order to ensure the presence of microfibrils in the gel in the first and second embodiments, but the shear stress must not be so great as to produce discrete fibers as in the process of our Application No. 1,287,917.

When the olefin polymerization reaction or

polyolefin dissolution is carried out under the conditions discussed herein, a fibrous gel material is ultimately obtained. "Fibrous" gel is defined as a fibrillar structure of fibrous polyolefin defining a network of interconnecting capillary spaces filled with the reaction medium. By "fibrous" polyolefin, it is intended to include both microfibrous polyolefin and macrofibrous polyolefin, as well as fibers. Generally, therefore, the polymer in the gel is in the form of microfibrils, macrofibrils, fibers and lamellae, and the proportion of these is dependent upon the history of the gel. Microfibrils may be obtained independent of any shear stress being imposed upon the reaction medium; however, the employment of shear stress in the medium tends to align the microfibrils into macrofibrils and fibers, and it is preferred to operate the process so as to form such macrofibrils and fibers. As previously mentioned, by "macrofibrils" it is intended to mean microscopic fibers having a diameter greater than about 1 micron up to about 20 microns, and microfibrils are microscopic fibers having a diameter less than about 1.0 micron.

The fibrous gel of the present invention is preferably made up of 3-30% by weight of the polyolefin, with the remainder being the reaction medium, minor amounts of catalyst and whatever is employed to stop the polymerization reaction, such as ethyl or isopropyl alcohol.

Wherever polyolefin polymer is referred to herein as being "crumb", it is intended to mean non-fibrous polyolefin particles.

Olefinic monomers which may be polymerized to form the fibrous gel of the present invention are any of those which can be polymerized by the employment of a coordination type catalyst. The preferred monomers are the monoolefins ethylene and propylene. Other olefins which may be employed are diolefins such as butadiene and isoprene and alpha olefins having a maximum of 18 carbon atoms per molecule such as 1-butene, 1-pentene, 1-dodecene and 4-methyl, pentene-1. In addition to forming fibrous homopolymers of the foregoing olefins, fibrous copolymers and block copolymers may be formed by the employment of mixtures of the foregoing olefins.

Any of these coordination type or stereospecific catalyst systems employed in the art for the polymerization of olefinic monomers may be employed for forming the polyolefin present in the gel made by the process of the present invention. Especially preferred are the Ziegler type coordination catalyst systems, which are generally a combination of a catalyst and co-catalyst. The catalyst is a compound (usually an oxide or halide) of a transition metal from groups IVB-VIIB and group VIII of the periodic table, and the co-catalyst is a metal alkyl where the metal is from groups IA, IIA, IIB or IIIA of the periodic table. The periodic table referred to is that in "Hand-

book of Chemistry", by Lange, seventh edition, pps. 58—59. Any conventional Ziegler type catalyst system, such as those described in Belgian patents 533,362; 534,792; and 534,888, may be employed in the present process. Three component Ziegler type catalysts may also be employed, and appear to have special utility where propylene is the olefinic monomer.

The preferred Ziegler catalysts and co-catalysts for polymerizing ethylene are as follows: preferred catalysts, in order of increasing activity in fiber formation, are titanium trichloride, titanium tetrachloride, vanadium tetrachloride and vanadium oxytrichloride; preferred co-catalysts, in order of increasing activity, are dialkyl aluminum halides such as diethyl aluminum chloride and trialkyl aluminum compounds such as triethyl aluminum.

The ratio of co-catalyst to catalyst (i.e. aluminum: titanium or aluminum: vanadium) employed is preferably in the range of 1:1 and 3:1, although ratios as low as 0.4:1 and as high as 50:1 or higher (with vanadium catalysts) are employable.

The preferred coordination catalyst systems and ratios for polypropylene and other olefinic monomers are those generally recognized in the art to give high reaction rates.

The catalyst concentration employed in the reaction medium is not per se critical to gel formation, the important thing being that sufficient monomer is presented to the polymer propagation sites on the catalyst to insure a relatively rapid rate of polymer formation.

More specifically, it is necessary that the rate of reaction per active catalyst site is high. The amount of monomer transported to such catalytic sites depends upon numerous factors such as temperature, degree of agitation of the reaction mass and monomer concentration, which in the case of gaseous monomers is dependent on the partial pressure of monomer in the system. Where the degree of agitation is relatively low or no agitation is employed, and the pressures employed are atmospheric or relatively low super-atmospheric pressures, it may be necessary to lower the catalyst concentration in the reaction medium in order to increase the rate of reaction per catalyst site to the level where microfibrils are formed in the resulting gel. Under conditions of relatively low or no agitation and relatively low monomer concentration, catalyst concentrations as low as about 0.005 millimoles per liter are satisfactory to effect microfibril formation. At higher monomer concentrations, the concentration of catalyst may be increased to as high as about 100 millimoles per liter. At 35—50 atmospheres, and low catalyst concentrations, fibers of polyolefins can be obtained with viscosity average molecular weights in the range of 10 million to 20 million.

While the Ziegler type coordination catalyst is preferred, other types of coordination cata-

lysts are also suitable. Exemplary of these other types of coordination catalysts are the Phillips catalysts and the catalysts of the Standard Oil Company of Indiana. The Phillips solution process is described in U.S. Patent 2,825,721; the Phillips slurry process is described in British Patent 853,414. The Standard Oil process is described in U.S. Patents 2,691,647; 2,726,231; 2,726,234; 2,728,758; 2,773,053; 2,791,575; 2,795,574; and 2,834,769.

The pressure employed in the polymerization reactor to form the fibrous gel may be any pressure conventionally employed for the particular type of olefin to be polymerized and the coordination catalyst used. However, it may be desirable to employ a higher pressure than conventionally employed in order to increase the reaction rate. Thus, if a Ziegler type coordination catalyst is employed, and the olefin is ethylene or propylene, pressures conventionally employed in the art are generally from subatmospheric up to about 100 atmospheres; for the process of the present invention such pressures may also be employed, but if it is desired to increase the reaction rate and form polyolefins having viscosity average molecular weights of 10 million to 20 million or higher, the range of pressures employed may be 35 to 50 atmospheres or higher. For the Phillips solution and slurry processes, pressures may typically range up to 35 atmospheres. In the Standard Oil polymerization process, pressures in the range of 35—105 atmospheres are typically employed.

The temperature employed in the polymerization reactions of the present invention is maintained between about the freezing point of the solvent up to the decomposition temperature of the solvent or polyolefin to be formed.

For the low temperature, non-solution process the temperature employed may range from the freezing point of the solvent up to the melt dissolution temperature of the polyolefin to be formed; it is generally preferable to operate between about 20° and about 110°C. for the most conditions and monomers.

For the high temperature, solution process (the second and third embodiments discussed above), the temperature employed in the polymerization reaction or for dissolving the pre-formed polymer is maintained between about the melt dissolution temperature of the polyolefin polymer to be formed and the decomposition temperature of the solvent or polymer. It is preferred to operate between the melt dissolution temperature and that temperature at which the polyolefin microfibrillar structure is destroyed. This temperature, which shall be called the "temperature of molecular randomization", is the temperature at which birefringence of the polymer solution disappears and can be determined by use of conventional techniques. If the temperature of poly-

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merization or temperature of dissolution of a preformed polyolefin is above the temperature of molecular randomization, it has been found that the polyolefin solution must be subjected to an increase in shear stress during cooling in order to form a satisfactory fibrous gel. It is generally preferable to operate between about 110°C. and about 165°C. for polyethylene.

The melt dissolution temperature of any particular polyolefin in a solvent is easily determined. Low concentrations of the polyolefin (e.g., 0.1 and 1.0% by weight) are placed into the solvent in a vial, which is sealed and placed in an oil bath. The temperature of the oil bath is raised slowly (10°C./hr.) until the last trace of polymer disappears. This temperature is the melt dissolution temperature. For ultra-high molecular weight (about 10 million) polyethylene at low concentration (0.1% by weight) in cyclohexane, the melt dissolution temperature is 118.5±1.9°C. For a dilute solution of high molecular weight polypropylene in cyclohexane, the melt dissolution temperature is 130°C. At higher concentrations the melt dissolution temperature approaches the melting point of the polyolefin. Lowering of molecular weight lowers the melt dissolution temperature at a given concentration.

As is the case with the formation of polyolefin nascent fibers described in specification No. 1,287,917, the organic solvent reaction medium employed in the present invention is also important to the formation of fibrous gel. The medium employed must essentially meet the same requirements set forth in the aforementioned patent application. The medium employed should be a suitable reaction medium for the polyolefin to be formed during the polymerization reaction. By the term "suitable reaction medium," it is intended to mean a composition into which the polyolefin to be formed is swellable or soluble to a significantly measurable extent and does not interfere with the polymerization reaction. By the phrase "significantly measurable extent," is meant that the measured amount of solvent absorbed by the polyolefin at equilibrium or after some finite time of soaking in the solvent, is above that which could reasonably be classified as due to experimental error rather than actual absorption (about 0.5% by weight).

A more accurate characterization of a suitable reaction medium is the "solubility parameter (δ) of the "solvent". The cohesive energy density is especially useful for predicting the solubility and solvent sensitivity of polymers. Polyolefins are soluble only in those solvents whose solubility parameter or cohesive energy density is not too far different from their own.

A detailed discussion of solubility parameter and cohesive energy density is set forth in specification No. 1,287,917, and in the book "Polymer Handbook", edited by Brandrup and Immergut, Interscience Publishers, 1966, pps. IV-341-68; and in "Encyclopedia of Polymer Science and Technology", Vol. 3, Interscience Publishers, pps. 833-62.

In order to qualify as a suitable reaction medium for forming a gel of polyethylene macrofibrils, the reaction solvent chosen should be as close as possible to the 7.7-8.35 (cal/cc)^{1/2} solubility parameter range of polyethylene, preferably between 6.5 and 9.5 (cal/cc)^{1/2}, and probably should not be outside the range of 6.0-10.0 (cal/cc)^{1/2}.

The solubility parameter of polyethylene at any temperature "T" can be determined by the following equation:

$$S_{T^{\circ}} = 8.4822 - 0.00642 \times (T^{\circ}C)$$

Similarly, the reaction medium chosen for polypropylene gel fiber formation should have a solubility parameter approaching 7.9-8.2 (cal/cc)^{1/2}. The preferred range is between 6.5 and 9.5 (cal/cc)^{1/2}, and probably should not be outside the range of 6.0-10.0 (cal/cc)^{1/2}.

Solubility parameter values for polyolefins other than polyethylene and polypropylene are to be found in Table 4, pages IV-362-67 of "Polymer Handbook", cited above, or can be calculated as set forth in specification No. 1,287,917. It should be noted that the solubility parameters set forth in "Polymer Handbook" are calculated from the heats of vaporization at 25°C., and that different values will be obtained at more elevated temperatures. At such elevated temperatures, the solubility parameter may approach close enough to that of the polyolefin to be formed to be a useful reaction medium, whereas at lower temperatures it would not be useful. An alternative approach to the definition of solubility characteristics of solvents useful in the practice of the present invention is the difference in solubility parameter ($\delta_s - \delta_p$) of the solvent and polyolefin. The heat of mixing of solvent and polyolefin is dependent upon the quantity ($\delta_s - \delta_p$)². If the heat of mixing is not so large as to prevent mixing, then ($\delta_s - \delta_p$)² has to be relatively small. For polyethylene it has been determined that ($\delta_s - \delta_p$)² should desirably be less than 3.0 (cal/cc) for fibrous gel formation, and preferably less than 1.5.

While the reaction medium chosen should preferably have a solubility parameter approaching that of the polyolefin to be formed, for polyolefins other than polyethylene the reaction medium thus chosen should not have a solubility parameter so close to that of the polyolefin as to cause dissolution of the microfibrils. This precaution does not apply to polyethylene because of its large enthalpy of fusion,

whereby there is no problem of microfibril dissolution below the melt dissolution temperature. However, for other polyolefins having a small enthalpy of fusion, any microfibrils formed may be quickly dissolved if the solubility parameter of the reaction medium is substantially the same as that of the polyolefin being formed.

Upon completion of polymerization in the high temperature, solution process, the polyolefin solution is cooled to a temperature below the melt dissolution temperature of the polyolefin to form a fibrous gel. The rate of cooling is not critical to formation of fibrous gel and can vary over a wide range of from as low as about 1/20°F. a minute to as high as 25°F. a minute or higher. It is not necessary that the cooling rate be constant. It is preferred to employ a slower cooling rate since this results in longer fibers. For example, at a cooling rate of 4°F. per minute, fibers average 10—15 mm in length, whereas at a cooling rate of 18°F. per minute, all fibers are very fine, being no longer than 0.05 mm in length.

In specification No. 1,287,917, it is disclosed that one of the principal factors contributing to the formation of polyolefin nascent or free-floating fibers is the shear stress to which the reaction mass is subjected during polymerization.

In the low temperature, non-solution process, the formation of such nascent fibers during the polymerization reaction is to be avoided since it is desired to postpone the formation of fibers until after the polymerization reaction is completed. Therefore, the shear stress to which the reaction mass of the present invention is subjected is lower than that which would form nascent or free-floating fibers and, in fact, fibrous gel made up of microfibrils and lamellae alone may be formed at zero shear stress. It is difficult to give an absolute figure for the maximum shear stress that may be employed and still obtain a fibrous gel rather than free-floating fibers since this maximum shear stress is dependent upon several reaction conditions, one of the more important of which is temperature. The probable minimum shear stress stated in specification No. 1,287,917 for nascent fiber formation was in the range of 0.1—1.5 pounds (force)/sq. ft. for most reaction conditions and most olefins. However, the maximum shear stress for forming fibrous gel and short of forming nascent fibers may be much higher than 1.5 pounds (force) sq. ft. at higher temperatures, and especially in the high temperature solution procedure for forming fibrous gel. Typical reaction conditions at various degrees of shear stress are set forth in Examples 6 and 13.

In the high temperature, solution process of the present invention the formation of fibers during the polymerization reaction is not possible since they would be dissolved, if formed.

Therefore, the shear stress to which the reaction mass of the present invention is subjected during polymerization in the solution process is not critical, and no shear stress need be employed.

However, in the solution process, it is desirable during cooling of the polyolefin solution to subject the solution to shear stress to effect fibrous gel formation. It is not essential to subject the solution to shear stress where the polyolefin has been formed in the reaction medium, but where the polyolefin is performed and subsequently dissolved, or where the polyolefin is formed above the melt dissolution temperature and subsequently raised above the temperature of molecular randomization, or where the polyolefin is formed initially above the temperature of molecular randomization, it is essential that the solution be subjected to shear stress upon cooling to effect satisfactory fibrous gel formation. This will be shown in the specific examples.

It has also been found that the type of shear stress to which the reactor mass is subjected in the low temperature process is important and it appears that laminar flow in the zones adjacent to the stirring mechanism is highly desirable. Chopping of the gel such as takes place in a polymerization reactor employing blender type blades induces too much turbulence into the reaction medium to permit gel formation.

The polymerization of olefin to polyolefin must be relatively rapid in order to form a fibrous gel instead of crumb.

The reaction rate per unit of catalyst, or apparent specific reaction rate, may be mathematically described by the expression

$$\frac{dM}{C \, dt}$$

wherein "M" is monomer consumed in millimoles, "t" is time in seconds, and "C" is amount of catalyst (transition metal halide) in millimoles.

The apparent specific rate is dependent upon the catalyst type, concentration of monomer in the reaction medium, temperature and pressure.

Since the minimum apparent specific rate necessary to form fibrous gel from any particular olefin is dependent upon all of the aforementioned variables, an absolute value therefor cannot be set forth without reference to a specific set of these variables. The minimum apparent specific rate required for fibrous gel formation for a particular olefin and catalyst system at any particular temperature and pressure must be determined for each set of variables chosen within the limits of each variable as specified herein. Since a selection of olefin, catalyst, temperature and pressure leaves monomer concentration in the reaction medium as the remaining variable determining the

apparent specified degree, it is usually this variable in practice which determines whether or not the minimum rate for fibrous gel formation is achieved. Once these other variables are chosen, the concentration of monomer in the medium depends upon the degree of pre-saturation of the medium (where the monomer is gaseous), the rate of monomer being fed into the medium, the nature of the medium (solubility of monomer therein) and the degree of agitation of the medium (dispersion of monomer therein). Since it is preferable to saturate the reaction medium with the monomer in the case of gaseous monomers prior to introduction of the catalyst, and since the monomer is usually fed into the medium in an excess amount during polymerization, and since the reaction medium itself is chosen within the parameters previously discussed, in practice the apparent specific rate is principally adjusted by the degree of agitation. However, as mentioned previously, the degree and type of agitation (shear stress) should not be such as to effect nascent fiber formation, as disclosed and claimed in specification No. 1,287,917.

This is not to say that the other variables cannot be employed in practice to obtain a reaction rate sufficiently high to effect gel formation, especially where no agitation (zero shear stress) is employed. For example, if it is determined that for a particular set of chosen variables the shear stress must be so high as to cause nascent fiber formation, then the temperature or pressure of the system may be adjusted to increase monomer solubility in the reaction medium, thereby increasing monomer concentration and raising the apparent specific rate. Alternatively, a more active coordination catalyst may be substituted to thereby increase the apparent specific rate. Further, a reaction medium having a smaller $(\delta_a - \delta_p)^2$ could be chosen to lower the minimum apparent specific rate required for gel formation, as is discussed elsewhere herein. A number of examples of apparent specific rates for various reaction conditions are set forth in the specific examples contained herein.

Figure 7 illustrates graphically the relationship between apparent specific reaction rate and solvent $(\delta_a - \delta_p)^2$ at various temperatures for polymerization of ethylene. For any given solvent and temperature, the minimum apparent specific reaction rate necessary to form fibrous gel may be generally determined from the graph. Any value of apparent specific reaction rate above this minimum value will form fibrous gel. The only upper limit on reaction rate is the practical one imposed by the catalyst, monomer concentration, temperature and pressure. Also, if the apparent specific reaction rate is being adjusted upwardly by increasing the degree of agitation, the degree of agitation (shear stress) should not be so great as to cause nascent fiber formation.

It is seen by reference to Figure 7 that the "better" the reaction medium (i.e., for the smaller values of $(\delta_a - \delta_p)^2$, the lower the reaction rate required to effect fibrous gel formation. Also, it is seen that higher temperatures promote fibrous gel formation by lowering the reaction rate required therefor.

It has been determined that the minimum apparent specific reaction rate necessary for gel formation where the polymerization is carried out close to the melt dissolution temperature of polyethylene in a very "good" solvent (decalin, $(\delta_a - \delta_p)^2 = 0.01$), is about 0.05 to 0.10 sec⁻¹. This may be taken therefore as the absolute minimum apparent specific reaction rate generally necessary to effect fibrous gel formation when operating below the melt dissolution temperature of the polyolefin to be formed.

An indication of the relatively rapid reaction rate involved in the present process is illustrated in Figure 5, wherein a polymerization reaction involving ethylene is carried out at various temperatures, and polymer yield is plotted versus reaction time. It is seen that while polymerization continues beyond the 12-minute time ordinate, gel formation is essentially completed during the first 2-4 minutes at all temperatures. It has been found that due to the high reaction rates involved in the polymerization of olefins to polyolefin fibrous gel and the upper limit of about 30% polymer in the gel, the reaction can in all cases be substantially completed within 30 minutes in a batch process, which is also quite close to the residence time involved in a continuous process. Details of the process conditions upon which the curves of Figure 5 are based are set forth in Example 9.

The polymerization reaction rate is not critical for fibrous gel formation in the high temperature, solution process. Since the reaction is carried out above the melt dissolution temperature, the reaction rate has been found to be, inherently, high enough to effect fibrous gel formation upon cooling. However, it has been found that fiber properties are effected by reaction rate. In general, it has been found that fiber strength properties are improved with an increase in reaction rate.

After formation of the fibrous gel, the gel is refined to liberate and/or form discrete fibers of polyolefin therefrom. The word "refined" as employed for this step of the process is not intended to mean the ultimate preparation of the fibers for their end use, such as in making nonwoven webs or in spinning yarns. The phrase "refined" as employed herein is intended to mean that step wherein polyolefin fibers are liberated and/or formed from the gel.

Refining is accomplished by subjecting the fibrous gel to a shear stress great enough to liberate and/or form fibers therefrom. The minimum shear stress required is dependent

upon numerous factors and an absolute value therefor cannot be stated without taking these factors into consideration. However, in general it is desirable that the shear stress be above about 0.1 to 1.5 lbs. (force)/sq. ft. The shear stress should not be so great as to detrimentally affect the fibers.

Refining is preferably accomplished by subjecting the gel to mechanical forces, preferably in the presence of reaction medium. This may be accomplished by the use of several types of apparatus such as the conventional type of disc refiners employed in the papermaking art. Other types of papermaking refining equipment suitable for forming and/or liberating the fibers from the gel include the PFI mill, Dyna Pulper and Jordans. The type of equipment employed is not critical, it being necessary only to impart to the fibrous gel sufficient mechanical forces or shear stress to liberate and/or form fibers therefrom. The magnitude of mechanical forces or shear stress necessary to accomplish this is readily determinable for the particular type of equipment employed. The only upper limit on the degree of agitation imparted to the gelatinous mass is that it should not be so high as to cause undue chopping of the fibers into a form which may be unsuitable for the ultimate end use.

Whereas the liberation of already formed fibers in the gel involves separation, the mechanism involved in the concurrent fiber formation from the microfibril and macrofibril portion of the polyolefin gel described hereby by such refining action is not completely understood. It is hypothesized that agitation of the gel during refining causes the microfibrils to align themselves into fibers. Microscopic analysis of the polyolefin fibers thus formed shows them to be made up of such macrofibrils.

Once the fibers are formed from the gel by refining, the reaction medium and catalyst may be removed therefrom by conventional techniques. Further mechanical treatment of the fibers to separate discrete fibers from fiber bundles may be effected by conventional defiberizing techniques, such as in a disc refiner. One of the unique features of the present process is that it provides fibers (after refining) which can have a sorbed solvent content at room temperature (20°C.) up to about 90% by weight of the total solvent-fiber mass. By "sorbed" solvent is meant solvent present as absorbed and adsorbed solvent. The amount of such sorbed solvent can be controlled by the amount of drying, solvent extraction, mechanical expression, steam distillation, or other conventional means of solvent removal from the fibers obtained after the refining step. The presence of such sorbed solvent has been found to aid fiber bonding and it is preferable to have a minimum of 1/2% by weight (20°C) retained for this purpose. However,

once the solvent is removed, it cannot be resorbed to provide the same degree of fiber bonding.

The viscosity-average molecular weight (\bar{M}_v) of the polyolefins produced in the present process ranges up to about 20 million and above, preferably between about one-half million to about 20 million in view of the improved strength properties over fibers of lower molecular weight polyolefins. The molecular weight can be controlled to any value desired in the conventional manner of employing chain termination agents. However, if the molecular weight (\bar{M}_v) falls below a certain minimum value, which for polyethylene and polypropylene is about 40,000 to 250,000, fibers will not be obtained upon refining. Therefore, it is generally very desirable to carry out the polymerization in the absence of any chain transfer agent.

The range of molecular weight distributions of the linear polyolefins such as polyethylene produced by the present process (as measured by the ratio of the weight-average molecular weight (\bar{M}_w) to number-average molecular weight (\bar{M}_n)) appears to be within the range reported in the literature for most common commercial grades. For example, a typical polyethylene produced by the present process (Table 6, run 6) has been found to have a molecular weight distribution (\bar{M}_w/\bar{M}_n) of 1.4.

The density range of the polyolefins obtained by the present process appears to be somewhat broader than that normally obtained by polymerization with a coordination catalyst. For example, polyethylenes are obtained having a density in the range of 0.926—0.990 g./cc.

The crystallinity of the linear polyolefins obtained by the present invention appears to be somewhat lower than the crystallinity of most commercial molecular weight polyolefins. This may be due to the more bulky molecule of the very high molecular weight polyolefins obtained in the present invention. For example, the crystallinity of polyethylene obtained in the present process is typically between about 55 and 85, as determined by differential scanning calorimetric measurement.

One of the most distinguishing features of polyolefin fibers formed by the process of the present invention is the high surface area provided, due at least in part to the microfibrillar and macrofibrillar structure of the fibers. Staple polyolefin fibers typically have surface areas (as measured by the conventional BET gas adsorption technique) of much less than about 1.0 square meter/gram. For example, 3 denier melt spun polyethylene staple has a surface area of about 0.16 m²/gram. Cellulose fibers (Whatman No. 1 filter paper) have a surface area of about 1.0 square meter/gram. The polyolefin fibers of the present invention generally have a surface area greater than 1.0 square

meter/gram, generally higher than about 25 m²/gram, and as high as 100 m²/gram or higher.

The fibers made by the present invention are not completely uniform in cross section along the length thereof. This is an advantage over staple fibers, which have a uniform cross-section, because such non-uniformity contributes to the web forming properties of the fibers. A majority of the fibers of the present invention are oval or circular in cross-section, rather than ribbon-shaped.

When the fibers of the present invention are classified according to TAPPI standard test No. T-233 SU-64 using the Bauer-McNett classifier (having screens of 20, 35, 65, 150 and 270 mesh arranged in sequence), more than 50% by weight are retained on the 150 mesh or coarser screens. Polyolefin pulps may be made having an average diameter of a majority of the fibers (by weight) exceed about 10 microns; such pulps are particularly useful for making synthetic papers. The average length of a majority of the fibers (by weight) is greater than 250 microns. The average length to diameter ratio of the fibers is greater than 5:1, and a majority of the fibers (by weight) have a length to diameter ratio greater than 10:1. Fibers having a diameter up to 600 microns or higher and lengths up to 4 mm or more have been observed.

The fibers of the present invention have great utility in making non-woven webs, particularly by normal papermaking techniques wherein the fibers are deposited from an aqueous slurry upon a moving foraminous forming surface such as a Fourdrinier wire. It has been found that sheets formed from the fibers of the present invention have extremely high opacity, which is quite useful in printing and other types of paper. The fibers of the present invention may be mixed with cellulose fibers to improve the opacity of paper formed therefrom. A particularly useful mixture is up to 50% polyolefin fibers mixed with cellulose fibers.

Prior to discussing the specific details of examples illustrating the present process, a brief description of a suitable apparatus for carrying out the process of the present invention will be presented.

Reference is made to Figure 1 of the drawing in which reference numeral 10 refers to the reactor of the first type. The reactor 10 is comprised of a cylindrical reaction vessel 11 fitted with a ground glass collar 12. A resin kettle lid 13 is located on top of the reactor, sealing it from the atmosphere. Located inside the reaction vessel is a thermocouple well 14. Through the bottom of cooling jacket 25 and reaction vessel 11 is a shaft 15 attached at the outside end thereof to a variable speed motor 16 and having at the other end thereof inside the reactor a cylindrical agitator 17. Side arm 18 protrudes through the lid 13 into

the interior of the reactor and is fitted at the outside end with a serum cap 19 for catalyst addition via hypodermic syringe. Monomer inlet 20 traverses through the lid 13 and fitted with a rotameter 21 for measuring gaseous monomer flow rates. The end of monomer inlet conduit 20 located inside the reaction vessel is fitted at its extremity with a fritted glass dispersion tip 24 to effect dispersion of the gaseous monomer in the polymerizing solvent. Excess gaseous monomer is withdrawn from the reactor via conduit 22, which is likewise fitted with a rotameter 23 to measure the exit gaseous monomer flow rate. Reflux condenser 26 returns condensables to the reaction vessel 11.

A larger scale reactor 30 is illustrated in Figure 2. Reactor 30 is comprised of a generally cylindrical shaped vessel 31 having a flange 32 at the upper end thereof and flange 33 at the lower end thereof. A circular top plate 34 is attached to vessel 31, such as by bolts through the outer perimeter of the top plate and the upper flange 32. Similarly, a bottom plate 35 is attached to vessel 31 by suitable means, such as bolts extending through the outer periphery thereof and through the lower flange 33. Agitator shaft 36 extends through a centrally located hole 37 in upper plate 34, which said hole 37 is fitted with a mechanical seal assembly. The lower end of agitator shaft 36 is guided in its lower portion by glass-impregnated-Teflon foot bearing 38. Agitator shaft 36 is driven by suitable motor means 39. Rotors 40, 41, 42 and 43 are located along the length of agitator shaft 36. Each rotor has six blades which do not have any pitch. Alternatively, a cylindrical rotor 49 illustrated in phantom may be employed.

Reaction vessel 31 is surrounded by a jacket 44, wherein cooling or heating liquid may be circulated. Inlet conduit 45 permits introduction of reaction medium into the reaction vessel 31. Monomer is introduced through sparger 46, and excess monomer exits through outlet 47. Serum cap 48 permits introduction of the catalyst and other materials in small quantities into the reaction vessel 31. A thermocouple not illustrated may be inserted into the reaction vessel at any suitable location to monitor temperature.

In operation the reaction vessels of Figures 1 and 2 were first flushed with nitrogen and then the reaction medium introduced. In the reactor of Figure 1, 1/2 liter of reaction medium was employed in the examples, whereas one gallon of reaction medium was employed in the reactor of Figure 2, unless otherwise noted. The reaction medium was then saturated with the olefin monomer, and a slight positive pressure maintained in the reaction vessel with monomer. The catalyst was next added via the serum cap, with the aluminum alkyl being added first. Where agitation was employed it was maintained throughout the

polymerization. Polymerization was quenched by injecting isopropanol (Figure 1) or ethanol (Figure 2) into the reaction medium via the serum cap.

The catalysts themselves were prepared in the manner conventional in the art. Reference is made to specification No. 1,287,917 and to the previously cited patents on the Ziegler, Phillips and Standard Oil processes, as well as standard texts for further description on catalyst preparation.

The reaction medium employed may be any of those solvents meeting the solubility parameter criteria described previously. Exemplary of suitable solvents employable as the reaction medium in the process for forming gels of polyethylene and polypropylene are cyclohexane, decalin, heptane, tetralin, chlorinated solvents, toluene, n-octane, isooctane, m, o and p-xylene, mineral oils, Socal 1 (a mixture of normal and branched aliphatic hydrocarbons, naphtha and aromatics), aliphatic hydrocarbons such as hexane (p-cymene and mixtures thereof).

The examples which follow illustrate various aspects of the invention, but are not to be construed as limiting the invention more narrowly than is stated in the claims.

In all of the tables, the catalyst systems are identified by code as follows:

- 1 — $\text{VOCl}_3 + (\text{C}_2\text{H}_5)_3\text{Al}$
- 2 — $\text{VOCl}_3 + (\text{C}_2\text{H}_5)_2\text{AlCl}$
- 3 — $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$

In all of the tables, "catalyst concentration" refers to the concentration of transition metal halide.

In all of the tables, the solvents are abbreviated as follows:

- | | |
|---|--|
| i-C ₈ | = isooctane (2,2,4-trimethyl pentane) |
| c-hex | = cyclohexane |
| p-cy | = p-cymene |
| p-xy | = p-xylene |
| benz | = benzene |
| n-hep | = n-heptane |
| tol | = toluene |
| n-C ₁₄ | = n-tetradecane |
| dec | = decalin |
| tet | = tetralin |
| n-C ₈ | = n-octane |
| xy | = Matheson, Coleman & Bell reagent grad xylene |
| o-C ₆ H ₄ Cl ₂ | = ortho-dichlorobenzene |
| DMSO | = dimethyl sulfoxide |

The apparent specific reaction rate $\frac{C}{dt}$ reported in the examples employing the ap-

paratus of Figure 1 (e.g. examples 1, 2, 5 and 6) was determined by dividing the monomer consumption (in millimoles) by the actual time (in seconds) monomer is being used and the catalyst amount (in millimoles). The different $\frac{C}{dt}$ values for each time interval measured

are then weighted by the fraction of polymer produced in that interval, and an average $\frac{C}{dt}$ calculated. With the examples employ-

ing the apparatus of Figure 2 (e.g. examples 3, 4 and 9) the value of $\frac{C}{dt}$ was determined

by dividing the polymer yield (in millimoles) by total reaction time (in seconds) and catalyst amount in millimoles. The apparent specific reaction rate is referred to in all the examples as "reaction rate".

The shear stress reported in the examples for the low temperature procedure was calculated only where the rotor was a cylinder (either Figure 1 or Figure 2 configuration). The shear stress reported is the mean shear stress (τ mean) in the annular space between the rotor and the wall of the reaction vessel, and was determined by the following equation:

$$\tau \text{ mean} = \mu \cdot \left[\frac{dv}{dr} \right]_{\text{mean}} \cdot \frac{1}{8}$$

where

μ = reaction fluid viscosity (lb. mass/(ft. sec.))

g = gravitational constant

$$[v]_r = \frac{T \times g}{4\pi\mu L} \left(\frac{1}{r} - \frac{r}{R^2} \right)$$

where

T = measured net torque of rotor cylinder (ft.-lb. (force))

L = length of rotor cylinder (ft.)

r = radial distance into annular space (ft.)

R = radius of reaction vessel (ft.)

By the mean value theorem,

$$\left[\frac{dv}{dr} \right]_{\text{mean}} = \frac{[v]_{r_0}}{R - r_0}$$

where

r_0 = radius of rotor cylinder (ft.)

The shear stress reported in the examples for the solution procedure was calculated from experimentally measured torque values. The shear stress (τ) in the annular space between

the rotor and the wall of the reaction vessel was determined by the following equation:

$$\tau = \mu \cdot \left[\frac{dv}{dr} \right]$$

$$\frac{1}{g} = \frac{T}{2\pi r_c^3 L}$$

5 μ = reaction fluid viscosity (lb. mass/ft)

(sec.)

where g = gravitational constant

10 T = measured net torque or rotor cylinder ft.-lb.) (force)
 L = length of wetted rotor cylinder (ft.)
 r_c = radius of rotor cylinder (ft.)

15 In employing the foregoing equation to determine shear stress, the measured net torque is corrected to remove "dead load", i.e., the measured torque is reduced by that amount attributable to solvent and bearing drag.

20 The molecular weights reported in the examples are viscosity-average molecular weights (M_v).

The viscosity average molecular weights in the following examples were determined by the relationship

$$(\eta) = K M_v^a$$

25 where

30 (η) = intrinsic viscosity, and is determined by Martin's equation (set forth on p. 207 of the book "Addition Polymers" by D. A. Smith, Plenum Press, N.Y., 1968. In Martin's equation, the "k" for high density polyethylene has been determined empirically to be 0.63 and for polypropylene to be 0.81). The specific viscosity used in Martin's equation was usually first corrected for shear rate, using the relationship of Francis et al (J. Polymer Sci., 31, 453 (1958)).

35 K = constant, from literature
 a = constant, from literature. For polyethylene, the values of Chiang (J. Polym. Sci., 36, 91 (1959)) were used; for polypropylene, the values of Redlich were used (J. Polym. Sci. A1, (1963)).

40 Experimental viscosity measurements for use in determining viscosity average molecular weights in accordance with the foregoing equation were made in decalin at 135°C. using Ubbelohde No. 50 or 75 viscometers.

45 Fibers produced from various molecular weight polyolefins were formed into nonwoven sheets and tested for various parameters conventional in the papermaking art. These parameters are caliper (TAPPI Standard Test No. T411 os-68), opacity/and scattering coefficient (TAPPI Standard Test No. T425 m-60), breaking length (TAPPI Standard Test No. T-494), stretch (TAPPI Standard Test No.

10 T-494), rupture energy (TAPPI Standard Test No. T-494), and tear factor (TAPPI Standard Test No. T-220). The fibers were prepared for nonwoven web formation by suspending about 0.25 gram of the fibrous gel (dry weight of fibers) in about 300 ml. of isopropanol, beating for 5 seconds in a one-quart Waring blender at 10,000 rpm, refining for 4 minutes in a miniature disc refiner, with the gap set for 2 minutes at 0.057 inch and for 2 minutes at 0.014 inch at 8,000-10,000 rpm. The miniature disc refiner is merely a modified one-pint Waring blender wherein the blades are replaced with a disc 23.87 mm in diameter, 6.35 mm thick and having four equally spaced grooves, 20.32 mm long, 1.016 mm deep and 4.57 mm wide machined into the upper surface thereof whose center lines are offset 4.06 mm from the center of the disc, and which has stationary disc centered thereover and adjustable vertically up and down to vary the gap between the discs, the upper stationary disc having the same diameter as the moving, lower disc, is 8.89 mm thick and has six equally spaced holes extending therethrough from the upper surface to the lower surface, the holes being 6.35 mm in diameter and being located 11.93 mm from the center of the disc. To the resulting slurry of free-floating fibers is added 50 ml. of isopropanol, and the slurry drained by suction through a No. 54 Whatman filter paper placed on top of a wire mesh screen 72 mm in diameter removably located at the bottom of a stainless steel cylinder 10 cm. high, the slurry being stirred prior to removal of the isopropanol with a perforated stirrer. The resulting nonwoven web is placed between standard TAPPI blotters and pressed for 3 minutes at 118 pounds per square inch of sheet. The filter paper is removed from the handsheet, and the handsheet pressed at 185°F. (85°C.) at 31.25 pounds per square inch of sheet for 5 minutes. New blotters are employed and the nonwoven sheet pressed for an additional 5 minutes under the same conditions.

105 Examples of Low Temperature Fibrous Gel Preparation (wherein the polymerization temperature is below the melt dissolution temperature)

EXAMPLE 1. Different Solvents

110 The apparatus of Figure 1 and the general procedure involving this apparatus previously described were employed for polymerizing ethylene to form a gel from which polyethylene fibers could be made by subsequent refining. The catalyst, catalyst concentration, temperature apparent specific rate, solvent and solubility parameter are specified for each run in Table 1, below.

115 It will be noted that in run 1, the solubility parameter of isooctane is 6.52, which is on the

borderline of being a suitable solvent, and the limits previously mentioned) the greater must be the reaction rate in order to form gel instead of crumb. This is illustrated in Figure 7, previously discussed, wherein it is seen that for a given solubility parameter difference, either crumb or gel is obtained, depending on whether the reaction rate is fast enough. As a general rule of thumb, the poorer the solvent (within the

TABLE I
Different Solvents

Run No.	Polymerization Conditions										
	Catalyst	Catalyst Concentration (Millimoles/Liter)	Al/Ti or Al/V	Solvent	Temperature, °C.	Mixer Velocity (cm/sec)	Shear Stress, lb.(f)/ft. ²	Viscosity, centipoises	Sol Parameter (δ_s)	($\delta_s - \delta_p$) ² (cal/cc)	Reaction Rate (sec ⁻¹)
1	1	1.0	3:1	i-C ₈	56	237	0.0010	0.34	6.52	2.5	0.85
2	2	0.1	50:1	i-C ₈	55	327	0.0015	0.35	6.5	2.5	4.4
3	1	0.5	3:1	c-hex	55	500	0.0034	0.54	7.82	0.09	1.3
4	2	0.12	50:1	p-cy	58	224	0.001	0.40	8.03	0.05	2.2
5	1	3.0	3:1	p-xy	69	1080	0.0050	0.37	8.30	0.07	0.84
6	1	0.5	3:1	benz	29	562	0.0041	0.57	9.08	0.64	5.23

TABLE I (Continued)

Run No.	Polyethylene	Yield (grams)	% PE in gel	Surface Area, m ² /g	Density, g/cc	M _w × 10 ⁻⁴ (corrected for shear)	(η), dl/g (corrected for shear)	Molecular Weight × 10 ⁻⁴ (uncorrected for shear)	Description of Product	T _m , °C	Percent Crystallinity	Tappi Opacity, handsheet
1	0.9	1.3	—	28.0	0.992	0.47	4.3	0.4	crumb	129		—
2	0.8	5.8	59.7	0.954	3.01	14.9	2.8	gel*	gel*	132		97.5
3	0.8	7.7	33.1	0.948	1.46	9.2	1.3	gel**	gel**	130	76	86.7
4	1.1	5.4	39.0	—	0.69	5.5	0.7	gel**	gel**	132		63.0
5	4.4	12.5	25.0	0.945	1.34	8.6	1.3	gel***	gel***	130		96.3
6	14.0	5.0	13.8	0.932	2.99	14.8	2.8	crumb	crumb	134		96.0

* — No visible fibrous structure
 ** — Some fibrous structure
 *** — Very fibrous structure

These descriptions are used in all tables.

Note: In all tables the percent crystallinity of the polyethylene fibers and the nonfibrous polymer (crumb) was obtained by measuring the enthalpy of melting with a Perkin DSC-1 B differential scanning calorimeter at a scanning rate of 2.5°C/Minute. The value obtained was then divided by 68.4 calories per gram, the value for 100% crystalline polyethylene. The crystalline melting points (T_m) were taken as the peak of the enthalpy curve.

EXAMPLE 2. Different coordination catalysts are employed to illustrate that polyolefin gel formation is not catalyst specific. Again, the apparatus of Figure 1 and the catalyst specific procedure previously described were employed.

TABLE 2

Run No.	1	2	3
Catalyst	1	2	3
Catalyst Concentration (millimoles/liter)	0.5	0.12	5.0
Al/Ti or Al/V	3:1	50:1	1:5
Solvent	c-hex	p-cy	dec
Temperature, °C.	55	58	88
Mixer Velocity (cm/sec)	500	224	444
Shear Stress, lb. (f)/ft. ²	0.0034	0.001	0.0057
Viscosity, centipoises	0.54	0.40	1.0
Sol Parameter (δ_s)	7.82	8.03	7.96
($\delta_s - \delta_p$) ² (cal/cc)	0.09	0.05	0.002
Reaction Rate (sec ⁻¹)	1.3	2.2	0.1
Polymer Yield (grams)	0.8	1.1	4.8
Molecular Weight $\times 10^{-6}$	1.3	0.67	—
Description of Product	gel**	gel**	gel***
% PE in gel	7.7	5.4	3.0
Surface Area, m ² /g	33.1	39.0	17.4
Tappi Opacity, handsheet	87	63	81
Scattering Coefficient	—	—	419
Density, g/cc	0.948	—	—
$M_v \times 10^{-6}$ (corrected for shear rate)	1.46	0.69	1.11
(η) dl/g (corrected for shear rate)	9.2	5.5	7.6
T _m °C.	130	132	132
Percent Crystallinity	—	76	—

EXAMPLE 3.

Different Catalyst Concentrations
The apparatus illustrated in Figure 2 and the general procedure therewith previously de-

scribed was employed for the runs tabulated below in Table 3, illustrating different catalyst concentrations for gel formations.

TABLE 3

Run No.	1	2	3	4
Catalyst	1	1	1	1
Catalyst Concentration (millimoles/liter)	0.05	0.10	0.30	1.65
Al/V	3:1	3:1	3:1	3:1
Solvent	c-hex	c-hex	n-hep	c-hex
Temperature, °C.	60	76	11	60
Mixer RPM $\times 10^{-3}$	1.4	1.4	1.4	1.4
Sol Parameter (δ_s)	7.7	7.5	7.6	7.7
($\delta_s - \delta_p$) ² (cal/cc)	0.12	0.22	0.59	0.12
Reaction Rate	38.6	18.0	11.4	4.0
Polymer Yield (grams)	37.0	34.5	66.0	129.0
Surface Area, m ² /g.	33.7	3.9	19.3	15.0
Tappi Opacity, handsheet	94.0	—	—	90.5
Scattering Coefficient	1180	—	—	697
Density, g/cc	0.934	0.935	0.929	0.938
$M_v \times 10^{-6}$ (corrected for shear)	6.4	2.97	2.54	1.5
(η) dl/g (corrected for shear)	24.3	14.27	13.3	9.5
Molecular Weight $\times 10^{-6}$	—	—	2.35	2.0
Description of Product	gel***	gel***	gel***	gel*** & sheets
T_m , °C.	134			135
Percent Crystallinity	82			72

EXAMPLE 4.

Different Temperatures
The apparatus illustrated in Figure 2 and the procedure associated therewith previously described were employed for polymerizing ethylene into a fibrous gel at different temperatures. The specific reaction conditions are set forth in Table 4 below, and show a tendency for gel formation to occur more readily at higher temperatures, i.e. above about 50°C.

While optimum gel formation is obtained at the higher temperatures, gel formation may occur at lower temperatures as is seen in run 3 of Table 3, runs 1 and 2 of Table 5, and runs 2, 3, 5 and 6 of Table 6. Reference is also made to Figure 6 of the drawings which illustrates optimum gel formation for the conditions specified therein at temperature between about 65—105°C.

Different Temperatures

TABLE 4

Run No.	Polymerization Conditions						
	Catalyst	Catalyst Concentration (millimoles/liter)	Al/V	Solvent	Temperature, °C.	Mixer, RPM $\times 10^{-3}$	Sol Parameter (δ_s)
1	1	0.05	3:1	c-hex	10	1.4	8.4
2	1	0.3	3:1	c-hex	15	1.4	8.3
3	1	0.3	3:1	c-hex	30	1.4	8.1
4	1	0.3	3:1	tol	48	1.4	8.6
5	1	0.05	3:1	c-hex	60	1.4	7.7
6	1	0.1	3:1	c-hex	76	1.4	7.5
							0.22
							18.0
							26.1
							23.6
							8.9
							14.9
							38.6
							Reaction Rate (sec^{-1})

TABLE 4 (Continued)

Run No.	Polyethylene	Polymer Yield (grams)	Molecular Weight $\times 10^{-4}$ (not corrected for shear)	Description of Product	Surface Area, m ² /g	Tappi Opacity, handsheet	Scattering Coefficient	Density, g/cc	$M_v \times 10^{-4}$ (corrected for shear)	(η) dl/g (corrected for shear)	T _m , °C	Percent Crystallinity
1	25.0	1.4	Free Fibers	25.4	18.3	92.0	—	0.926	7.67	27.9	133	72
2	136.0	7.4	Free Fibers	Free Fibers	21.4	91.5	—	0.928	6.0	23.8	134	66
3	51.5	2.9	Long	Free Fibers	15.6	—	—	0.926	7.7	28.0	134	82
4	86.0	7.0	Free Fibers	Free Fibers	33.7	94.0	1180	0.934	6.4	24.3	134	
5	37.0	—	gel***	gel***	3.9	—	—	0.935	2.97	14.27		
6	34.5	—	gel***	gel***								

EXAMPLE 5

Different Reaction Rates

The apparatus illustrated in Figure 1 and the general procedure associated therewith were

employed in polymerizing ethylene at the conditions specified in Table 5, below. It is seen from the table that at lower reaction rates crumb is obtained, rather than a fibrous gel.

TABLE 5

Run No.	1	2	3
Catalyst	1	1	1
Catalyst Concentration (millimoles/liter)	1.0	0.5	0.5
Al/V	3:1	3:1	3:1
Solvent	c-hex	c-hex	c-hex
Temperature, °C.	29	40	55
Mixer Velocity (cm/sec)	190	157	500
Shear Stress, lb.(f)/ft. ²	0.002	0.0014	0.0034
Viscosity, centipoises	0.81	0.68	0.54
Sol Parameter (δ_s)	8.1	8.04	7.82
($\delta_s - \delta_p$) ² (cal/cc)	0.009	0.03	0.09
Reaction Rate (sec ⁻¹)	0.7	1.0	1.3
Polymer Yield (grams)	2.6	0.8	0.9
% PE in gel	—	4.0	7.7
Surface Area, m ² /g	9.3	50.1	33.1
Tappi Opacity, handsheet	—	97.5	86.7
Scattering Coefficient	—	—	—
Density, g/cc	0.937	0.950	0.948
$M_v \times 10^{-6}$ (corrected for shear)	0.85	1.2	1.46
(η) (dl/g) (corrected for shear)	6.37	8.17	9.2
Molecular Weight $\times 10^{-6}$ (not corrected for shear)	—	1.2	1.3
Description of Product	crumb	gel*	gel**
T _m °C.	126	130	130

10

EXAMPLE 6.

Different Degrees of Shear Stress during Gel Formation

The apparatus illustrated in Figure 1 and the general procedure associated therewith previously described were employed for polymerizing ethylene under different degrees of shear stress during gel formation. It is seen by reference to Table 6, below, that fibrous gels were formed at various degrees of shear stress (including no shear stress) up to about 0.01 lbs. (f)/sq. ft. (run 6). Between about 0.01

15

25

20

30

(run 6) and 0.024 (runs 7 and 8), a transitional phase is illustrated where a swollen fiber aggregate is obtained. When the shear stress reached 0.62 lbs. (f)/sq. ft. (run 9), the shear stress was sufficient to cause nascent polyolefin fiber formation, rather than a fibrous gel. In run 9 the solvent was changed to Drakeol 19 (a white mineral oil manufactured by Pennsylvania Refining Co.) because of its heavier viscosity, thereby enabling a greater shear stress to be imparted to the reaction mass.

TABLE 2
Different Degrees of Shear

Run No.	1	2	3	4	5	6
Polymerization Conditions						
Catalyst	1	1	1	1	1	1
Catalyst Concentration (Millimoles/Liter)	0.05	0.5	0.1	0.5	0.5	1.0
Al/V	3:1	3:1	3:1	3:1	3:1	3:1
Solvent	C-hex	C-hex	C-hex	C-hex	C-hex	C-hex
Temperature, °C.	12	40	28	55	14	37
Mixer Velocity (cm/sec)	0	157	195	500	590	1145
Shear Stress, lb.(f)/ft. ²	0	0.0014	0.002	0.0034	0.0080	0.010
Viscosity, centipoises	1.17	0.68	0.8	0.54	1.07	0.715
Sol Parameter (δ_s)	8.4	8.04	8.3	7.82	8.41	8.0
($\delta_s - \delta_p$) ² (cal/cc)	0.002	0.03	0.008	0.09	0.0005	0.025
Reaction Rate (sec ⁻¹)	2.2	1.0	3.0	1.3	1.5	0.5
Polyethylene						
Polymer Yield (grams)	8.4	0.8	1.2	0.8	1.7	4.2
Molecular Weight $\times 10^{-6}$	—	1.2	—	1.3	1.6	—
Crystallinity (%)	76	—	80	—	—	—
Melting Point, °C.	133	130	136	130	132	—
Description of Product	gel*	gel*	gel**	gel**	gel***	gel***
% PE in gel	—	4.0	—	7.7	9.6	—
Surface Area m ² /g	37.1	50.1	2.2	33.1	45.9	19.4
Tappi Opacity handsheet	—	97.5	—	86.7	89.	—
Scattering Coefficient	—	—	—	—	—	—
Density, g/cc	0.935	0.950	—	0.948	0.934	0.933
$M_v \times 10^{-6}$ (corrected for shear)	3.49	1.2	1.3	1.46	1.6	3.55
(η) dl/g (corrected for shear)	16.44	8.17	8.7	9.2	9.77	16.6

EXAMPLE 7.

Refining the Fibrous Gel into Fibers
A fibrous polyethylene gel was prepared in the apparatus illustrated in Figure 2. The rotor employed was a 4-inch diameter 3 blade standard propeller, rotated at a peripheral velocity of 186 cm/sec. One and one-half gallons of cyclohexane were presaturated with ethylene at reaction temperature (82°C.). Triethylaluminum was added first to the reaction medium, followed by addition of vanadium oxytrichloride for a catalyst concentration of 0.10 millimoles per litre and an Al:V ratio of 6:1. After 10 minutes, ethanol was injected to kill the reaction. The apparent specific reaction rate was calculated to be 9.54 (sec⁻¹). The yield of gel was 91.1 grams and the viscosity average molecular weight was 3.08 x 10⁵. (η) = 15.1 dl/g. The polymer density was 0.96 g/cc.

The apparatus employed for carrying out the refining of the gel into polyethylene fibers is that illustrated in Figure 3 and known in the paper-making art as a disc refiner. One suitable type is manufactured by Sprout-Waldron. Other types of disc refiners such as those manufactured by Bauer Brothers may also be employed; this latter disc refiner is described in U.S. Patents 2,214,707 and 2,568,783.

In general, the disc refiner comprises a pair of refining discs 121 and 122 carrying removably mounted roughened surface refining plates sections 123 as shown in Figure 4; the roughened surface is formed by ribs 124. The rib pattern shown in Figure 4 is one of many different patterns that are available and is merely shown for purposes of illustration. The working space 126 between the discs is usually tapered toward the periphery. Ordinarily, fibrous gel is introduced by any suitable means into the working space 126 through inlet 127, adjacent the axis of rotation of the discs. Either one or both of the discs may be rotatable, and where they are both rotatable they usually rotate in opposite directions. In this example, the disc designated 121 was fixed and disc 122 rotated by virtue of the motor means partially illustrated. Disc 121 is yieldably mounted to permit adjustment of the working space between the discs by means of hydraulic piston 128, which is slidable into cylinder 129 and controlled by hydraulic control mechanism 131. The piston 128 is connected to a rod 132, slidable in bearing 133 and attached to disc 121. The limit of movement of yieldable disc 121 toward disc 122 is controlled by a stop nut 134 threaded on spindle 137, having a swivel connection at turning by means of a pin 139 projecting through an aperture 141 in the nut. By turning hand wheel 142, secured to spindle 137, the relative axial position of nut 134 with respect to spindle 137 can be adjusted to limit the forward movement of disc 121 and

thus provide control for the spacing between discs 121 and 122.

In the present example the disc refiner employed was manufactured by Sprout Waldron; the discs were 10" in diameter and bar type plates No. 17805 were used. These plates have a herringbone design. Valleys in the design were 3/16" wide, the raised areas 1/8" wide, and 1/8" high.

The fibrous gel slurry was preliminarily treated for 15 seconds with a Waring blender to break up the large gel mass into smaller gel pieces and then passed through the disc refiner three times. The refiner was operated at 900' per minute with clearances between the plates of 0.1" for the first time, 0.01" for the second, and 0.005" for the third. The material was then collected on a filter and redispersed in 10 liters of water, together with 2.5 milliliters of wetting agent (Zonyl A) and 5 milliliters concentrated hydrochloric acid, to a consistency of 0.25% (by weight). The thusly prepared fiber slurry was passed through the disc refiner as mentioned and collected on a 200 mesh screen.

The fibers obtained from the disc refining were screened through five 10-inch Tyler screens. The screens were stacked with the coarsest screen on top and the finest at the bottom. Ten grams of fiber from the disc refiner were dispersed in one liter of water and placed into the top screen. Water was then sprayed at a rate of 1200 milliliters per minute for a total time of 10 minutes. During this time the screen stack was shaken back and forth with a one-inch stroke. The results are set forth in Table 7, below.

TABLE 7.
Fiber Size after Refining Fibrous Gel

Screen Size	Fiber Portion Retained (%)
14 mesh	16
20 mesh	21
35 mesh	45
65 mesh	13
150 mesh	1
Through 150 mesh	4

The foregoing distributions of fiber size is quite similar to the fiber size distribution that would be obtained with cellulosic fibers employed for papermaking. The surface area was 7.4 m²/g.

EXAMPLE 8.

Refining Fibrous Gel with a Dyna Pulper
The Dyna pulper is not illustrated in the drawings but is a regular, conventional type of paper making equipment. It consists of a horizontally arranged cylindrical stainless steel vessel with a diameter of 10". The ends of the cylinder are slightly conical. Inside this cylinder are two discs arranged parallel to

63

Stress During Gel Formation

7	8	9	10	11	12	13
2	1	2	1	2	1	2
0.15	0.5	0.15	5.0	0.15	0.5	0.15
40:1	3:1	40:1	3:1	40:1	3:1	40:1
C-hex	C-hex	C-hex	decalin	C-hex	Drakeol 19	C-hex
64	65	51	56	61	55	63
1437	2850	167	1330	322	2638	345
0.013	0.017	0.24	0.024	0.58	0.62	0.65
0.5	0.47	0.60	1.44	0.5	18.4	0.5
7.7	7.69	7.88	8.29	7.7	6.6	7.7
0.13	0.14	0.07	0.028	0.13	—	0.13
8.0	3.2	12.0	0.07	9.0	—	9.7
3.5	0.8	4.4	5.6	3.4	23.5	1.5
—	1.6	—	4.2	—	1.9	—
—	—	—	80	—	—	—
—	131	—	136	—	—	—
gel***	Swollen Fiber Aggreg.	gel***	Swollen Fiber Aggreg.	Swollen Fiber Aggreg.	Nascent Fibers	gel***
8.4	9.0	10.0	—	16.0	6.	9.0
—	37.6	31.4	28.6	22.9	—	—
—	88.6	87	84.9	98	97.5	—
—	736.	667	575.	942	2011.	—
—	0.944	—	0.937	—	—	—
—	1.6	2.6	4.2	0.93	—	—
—	9.61	13.5	18.5	6.8	—	—

each other and 10" apart. The sides of these discs facing each other are studded with steel teeth of various sizes up to 3/8" high. During operation, the two discs counter-rotate to each other at 2,000 rpm.

The fibrous gel prepared in accordance with run 1 of example 3 was charged to the Dyna pulper in the form of three pieces of gel having a total weight of 80 grams. Refining was done in 8 liters of cyclohexane and the gel was exposed to the rotating discs for 20 minutes.

Bundles of fibers up to 2" long were obtained. The thickness of the bundles ranged from very thin bundles of only a very few fibers to bundles 0.125" thick. Such bundles would be further refined by conventional techniques to separate the individual fibers from the bundles (defibering) prior to using the fibers for textile applications or for non-woven webs, as in papermaking.

EXAMPLE 9.

Reaction Time

Ethylene was polymerized at various temperatures in the reactor illustrated in figure 2 except that agitation was effected with a single 3-blade rotor mounted on the shaft about 4 inches from the bottom. The rotor was operated at 350 rpm. The solvent was Phillips 85% grade cyclohexane for the runs at 125°F., and Phillips pure-grade cyclohexane for all other runs. The solvent was predried with a Linde 4A mol-sieve. The solvent was saturated with ethylene at reaction temperature and pressure prior to reaction initiation, and no ethylene was added after initiation, and no polymerization. The co-catalyst, triethyl aluminum, was added in excess to the reactor (at 0.6 gram-millimole/liter) to destroy any residual water in the system. The catalyst vanadium oxytrichloride, was then immediately added at 0.1 gram-millimole/liter. Reactor temperature was maintained for the 125°F. and 180°F. runs by circulating hot water of proper temperature through the reactor jacket. Pressurized steam was circulated for the 250°F. runs. Reaction time was that period between injection of vanadium oxytrichloride into the reactor to initiate the polymerization and the injection of ethanol to kill the reaction. Yield of fibrous gel was determined, and the results were plotted as illustrated in figure 5, with curve A being the 125°F. runs, curve B being the 180°F. runs, and curve C being the 250°F. runs. As discussed previously, these curves show that polymerization was essentially complete at the end of 2-4 minutes, indicating a relatively rapid reaction rate.

EXAMPLE 10.

Polypropylene Fibers

Propylene was polymerized in the reactor of Figure 2 to form a fibrous gel. Three rotors having no pitch were employed for agitation

and operated at 1400 rpm. One gallon of cyclohexane was introduced into the reactor and saturated with polypropylene at 60°C., and excess propylene passed through the reactor to maintain a pressure of 30 psi thereon. Diethyl aluminum chloride was added first to the reactor at a concentration of 1.5 millimole/liter, followed by the addition of 1.0 millimole/liter of vanadium oxytrichloride and, finally, 1.5 millimole/liter of triethyl aluminum, for a total ratio of Al:V of 3:1.

The reaction was continued for ten minutes and then terminated by addition of isopropyl alcohol. The solubility parameter of cyclohexane at the reaction temperature is 7.75, and $(\delta_s - \delta_p)^2$ is 0.0032 cal/cc. Fibrous polypropylene gel was obtained, and refined in a Waring blender at high speed. Polypropylene fibers were obtained.

The polypropylene fibers had a surface area of 4.3 m²/g. The viscosity average molecular weight of the fibers was 90,000 ($(\eta) = 0.9$ dl/g).

EXAMPLE 11.

Higher Pressure Runs

For producing polyolefin fibers at higher pressures, a steam jacketed, batch autoclave reactor of approximately one gallon capacity (Benco Model 575 RJ having a 1/4 horsepower variable speed type R drive) was employed. The warmed autoclave is purged for about 4 hours with nitrogen, and one gallon of cyclohexane (purified by running it through a molecular sieve column) introduced using nitrogen pressure to force it from the reservoir into the reactor. Steam was introduced into the jacket of the autoclave to bring the cyclohexane up to reaction temperature. Ethylene gas was then introduced to the reactor with a slight amount of venting through the relief valve to provide a small ethylene purge. The stirrer (a curved blade turbine having 6 blades 3 inches in diameter and a blade height of 3/8 inch) was operated at 1500 rpm. Ethylene introduction was continued until the pressure in the reactor remained constant, indicating saturation of the cyclohexane. The relief valve and ethylene inlet line were then closed. About 10 c.c. of cocatalyst (triethyl aluminum) dissolved in cyclohexane was introduced into a reservoir having a rubber septum via hypodermic syringe, and from the reservoir through a remotely controlled diaphragm operated needle valve into the reactor by nitrogen pressure slightly higher (about 100 psi) than the pressure in the reactor. After about 30 seconds mixing about 10 c.c. of the catalyst (vanadium oxytrichloride) dissolved in cyclohexane was introduced into the reactor in a similar manner. The ratio of cocatalyst to catalyst (TEAL/VOC₂) was 6/1. The introduction of the catalyst marks the beginning of the polymerization reaction. The reaction was terminated by injecting a catalyst poison (isopropanol) into the reactor in the same manner as the introduc-

tion of catalyst and cocatalyst. The steam was then turned off and cooling water (about 55°F) circulated in the jacket. After the reactor had cooled to about room temperature, the relief valve was opened and excess pressure relieved. The fibrous gel product was then removed from the reactor. The results are as follows:

TABLE 8

Higher Pressure Polymerization

Run No.	1	2
<u>Polymerization Conditions</u>		
Initial Pressure, atmospheres	20	37
Initial Temperature, °C.	55	53
VOCl ₃ (g./mole/liter)	0.026	0.026
Reaction time (minutes)	5	8
Maximum temperature (°C)	125	56
Reaction rate (Sec ⁻¹) *	219	9.9
<u>Polyethylene Properties</u>		
Yield (g)	183	13.5
Yield (g PE/g VOCl ₃)	10,600	780
M _v × 10 ⁻⁶	6.8	20.5
<u>Handsheet Properties</u>		
Breaking Length, meters	385	—
Tear Factor	68	—
Rupture Energy, ergs/cm ²	0.7 × 10 ⁴	—
Scattering Coefficient	234**	—

*Calculated in the manner previously described for reactor of Figure 2.

**Average of two handsheets tested.

Examples of High Temperature Fibrous Gel Preparation (wherein the Polymerization Temperature is above the Melt Dissolution Temperature)

Examples 12—19 below are all high temperature fibrous gel preparations wherein the polymerization was carried out above the melt dissolution temperature, or a preformed polyolefin dissolved in solvent above the melt dissolution temperature, and the resulting solution cooled to below the melt dissolution temperature to form a fibrous gel.

EXAMPLE 12.

Importance of Molecular Weight
This example illustrates the criticality of employing polyolefins having very high molecular weights to obtain fibers of suitable strength for preparation of satisfactory non-

woven sheets. Table 9A below shows the effect of molecular weight on polyethylene fiber sheets produced by polymerization of ethylene in the reaction media under the conditions stated. Table 9B below shows the effect of molecular weight where preformed polyethylene is employed in forming fibers. Table 9C below shows the effect of molecular weight where preformed polypropylene is employed in forming fibers.

It is seen from the foregoing tables that molecular weight of the polyolefin has an important effect on fiber properties. For polyethylene, the molecular weights of runs 1, 7, 8 and 9 give fibers on the borderline of satisfactory strength properties for use in nonwoven webs. For polypropylene, the molecular weights of runs 16, 17, 18 and 19 are on the borderline of giving satisfactory fibers.

20

25

30

35

Varying Molecular Weight (Polyethylene)

TABLE 9A

Run No.	Polymerization Conditions										Phase Change Conditions										*Apparent specific reaction rate $\frac{(\text{dm})}{(\text{C dt})}$																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
	Solvent	Catalyst	Catalyst Concentration (Millimoles/Liter)	Al/Ti or Al/V	Temperature, °C	Time (Min)	Pressure (psig)	Rotor Speed (rpm)	Reaction Rate (Sec ⁻¹)*		Temperature, °C	Rotor Speed (rpm)	Solution Viscosity, centipoises	Shear Stress, lb(f)/ft. ²	($\delta\sigma/\delta p$) ² cal/cc	Cooling Rate (°/min)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								

TABLE 9A (Continued)

Run No.	1	2	3	4	5	6
Polyethylene						
Yield (grams)	28.0	0.4	25.5	10.5	21.0	69.0
% Polyethylene (weight) in gel	—	—	4.0	—	—	12.0
Molecular weight $\times 10^{-5}$	0.30	0.51	0.66	1.4	1.86	2.15
Surface Area (m^2/g)	25.8	53.7	31.5	58.9	47.5	48.7
Description**	1	2	2	2	2	2
(η), dl/g	3.2	4.5	5.4	8.9	10.8	11.9
T _m °C	131	131	133	136	132	137
% Crystallinity	—	—	74	79	—	73
Handsheet Properties						
Caliper (mils)	5.8	—	4.3	4.4	5.9	4.6
Tear Factor	0	—	46.5	62.0	55.0	57.0
Breaking Length (meters)	589	962	1988	2177	1739	2070
Rupture Energy, ft.lbs./sq.ft.	0.1	0.9	6.8	65.7	32.5	24.7
Opacity, %	93	65	74	34	92	75
Scattering Coefficient, cm^2/g	781	139	264	66	801	286

**1 = Structureless gel
 2 = Fibrous gel
 3 = Crumb

These description codes are used in tables 9 — 12.

Notes: Runs 1—6 made in reactor of figure 2, cylindrical rotor. Use of — in tables indicates value not determined.

Varying Molecular Weight (Preformed Polyethylene)

TABLE 9B:

Run No.	Solution Conditions			Phase Change Conditions				Polyethylene			Description			(η) dl/g	T _m °C	Surface Area (m ² /g)
	Solvent	Polyethylene Concentration (%)	Temperature, °C	PE Molecular Weight $\times 10^{-6}$					Cooling Rate (%/min)	% Polyethylene (weight) in gel						
7	xy ^l	1.0	85	0.06	72	850	0.07	1.2	12.0	3	3	1.1	122	1.1	122	—
8	xy ^l	1.0	98	0.06	77	910	0.06	0.8	7.0	3	3	1.0	—	1.0	—	9.6
9	xy ^l	1.0	90-93	0.08	74	775	0.07	0.8	—	3	3	1.3	127	1.3	127	8.2
10	n-C ₁₄	1.0	105-108	0.17	88	900	0.04	0.9	5.0	2	2	2.2	127	2.2	127	15.8
11	xy ^l	1.0	114	0.23	98	957	0.46	—	10.0	2	2	2.7	120	2.7	120	3.9
12	xy ^l	1.0	94	0.44	93	740	0.03	1.1	5.0	2	2	4.1	125	4.1	125	24.5
13	xy ^l	1.0	90	0.77	84	750	0.04	1.9	5.0	2	2	6.0	127	6.0	127	14.5
14	xy ^l	1.0	92	0.95	86	860	0.04	1.0	7.0	2	2	6.8	126	6.8	126	33.9
15	xy ^l	1.0	>103	6.7	82	1000	0.05	1.9	5.0	2	2	25.1	130	25.1	130	20.9

TABLE 9B (Continued)

Run No.	Handsheet Properties					
	Tear Factor	Breaking Length (meters)	Rupture Energy, ft.lbs./sq.ft.	Stretch (%)	Opacity, %	Scattering Coefficient, cm ² /g
7	*	*	*	*	*	*
8	*	*	*	*	*	*
9	*	*	*	*	*	*
10	45	231	0.04	1.2	95	1171
11	100	1087	2.3	7.2	88	583
12	41	1422	2.8	6.8	85	469
13	45	1981	7.4	13.3	87	467
14	70	801	1.7	5.6	89	700
15	49	1180	2.4	4.9	92	584

*Too weak to test.

Note: Runs 7-15 made in reactor of figure 1.

TABLE 9C
Varying Molecular Weight (Reformed Polypropylene)

Run No.	Solution Conditions					Phase Change Conditions					Polypropylene				
	Solvent	Polypropylene Concentration (%)	(grams/ml) × 100	Temperature, °C.	PP Molecular Weight × 10 ⁻⁶	Temperature, °C	Rotor Speed (rpm)	(δ _s -δ _p) ² cal/cc	Cooling Rate (°/min)	% Polypropylene (weight) in gel	Description	(η) (dl/g)	Tm °C	Surface Area (m ² /g)	ΔH (cal/g)
16	dec	1.0	1.0	123	0.13	51	1140	0.34	3.9	—	3	1.3	167	3.9	38
17	n-C ₁₄	1.0	1.0	139	0.12	92	900	0.06	0.77	10.0	2 & 3	1.1	159	7.3	12
18	C-hex	1.0	1.0	—	0.12	42	1000	0.04	14.0	14.0	2 & 3	1.1	165	10.2	14
19	C-hex	1.0	1.0	—	0.16	44	1000	0.04	15.0	9.0	2 & 3	1.3	165	101.0	22
20	C-hex	1.0	1.0	—	0.46	40	1000	0.05	13.0	10.0	2 & 3	2.5	165	20.9	16.7
21	C-hex	1.0	1.0	—	0.57	54	1000	0.05	4.0	8.0	2 & 3	3.0	169	91.1	36

TABLE 9C (Continued)

Run No.	Handsheet Properties	Tear Factor	Breaking Length (meters)	Rupture Energy, ft.lbs./sq.ft.	Opacity, %	Scattering Coefficient, cm ² /g
16	*	0	835	0.1	*	401
17		13	1387	0.7	86	557
18		9	876	0.3	86	539
19		25	2185	3.0	79	383
20		—	2238	8.5	82	368
21						

*Too weak to test

Note: Runs 16 and 17 made in reactor of figure 1. Other runs (18—21) made in reactor of figure 2, cylindrical rotor.

EXAMPLE 13.

Varying Shear Stress

The runs reported in tables 10A and 10B show the effect on fibrous gel formation and fiber properties of varying shear stress during cooling of the polyethylene solution. As can be seen from table 10A, imparting shear stress to the polyethylene solution during cooling is not essential to fibrous gel formation where the polyethylene solution has been maintained below the molecular randomization temperature, but does aid in improving strength properties of the fibers produced therefrom. Table 10B shows that some shear stress is necessary where the polyethylene solution is heated above the temperature of molecular randomization. Run 31 was subjected to shear stress and formed a fibrous gel whereas Run 32 was not and did not form a gel but a floc. Run 33 illustrates that shear stress during polymerization is not essential.

Varying Shear Stress

TABLE 10A

Run No.	Polymerization Conditions										Phase Change Conditions						
	Solvent	Catalyst	Catalyst Concentration (Millimoles/Liter)	Al/V	Temperature, °C	Time (Min.)	Pressure (psig)	Rotor Speed (rpm)	Reaction Rate (Sec ⁻¹)		Temperature, °C	Rotor Speed (rpm)	Solution viscosity, centipoises	Shear Stress, lb.(f)/ft. ²	($\delta_s - \delta_p$) ² cal/cc	Cooling Rate (°/min)	
22	C-hex	1	0.1	6.1	138	60	100	0	0.82		—	0	—	0	0.69	3.2	
23	C-hex	2	0.5	12.1	138	4	100	90	5.0		113	70	3490	0.89	0.54	3.3	
24	i-C ₈	2	0.1	12.1	139	4	106	1100	8.3		93	1100	238	1.0	3.16	2.8	
25	C-hex	2	0.1	12.1	138	4	100	500	4.1		107	500	575	1.0	0.47	4.2	
26	C-hex	2	0.02	12.1	138	4	100	1200	9.9		110	500	733	1.3	0.51	13.4	
27	C-hex	2	0.1	12.1	138	4	100	200	7.2		—	200	2090	1.5	0.5	—	
28	C-hex	2	0.004	12.1	138	4	100	1100	15.0		104	900	581	1.9	0.44	16.6	
29	C-hex	2	0.1	12.1	127	15	120	1000	—		123	750	2360	6.2	0.54	0.5	
30	C-hex	2	0.1	12.1	138	4	100	1000	6.7		118	1000	1700	6.25	0.2	9.5	

TABLE 10A (continued)

Run No.	Polyethylene									
	Yield (grams)	% Polyethylene (weight) in gel	Description	Molecular weight $\times 10^{-4}$	Surface Area (m^2/g)	(η) dl/g	T_m °C	% Crystallinity	Handsheet Properties	
									Tear Factor	Breaking Length (meters)
22	11.8	—	1	1.33	24.8	8.6	131	—	26	1616
23	83.0	7.0	2	2.0	23.9	11.5	132	67	34	1745
24	21.2	—	2	1.86	47.5	10.8	132	—	54.5	1739
25	10.5	—	2	1.4	58.9	8.9	136	79	62	2177
26	5.0	5.0	2	1.48	67.2	9.2	137	76	79	2287
27	27.7	6.0	2	1.7	17.1	10.2	132	69	31	1746
28	1.5	22.0	2	2.8	53.1	14.0	139	59	184	1170
29	69.0	11.0	2	2.15	48.7	11.9	137	73	57	2070
30	25.5	6.0	2	0.66	31.5	5.4	133	74	47	1988
										Rupture Energy, ft.-lbs./sq.ft.
										Stretch (%)
										Opacity, %
										Scattering Coefficient, cm^2/g
22									26	530
23									34	334
24									62	800
25									79	66
26									76	264
27									69	281
28									59	358
29									73	286
30									74	264

Note: Runs 22-30 made in reactor of figure 2, cylindrical rotor.

TABLE 10B

Effect of Temperature and Shear Stress on Fibrous Gel Formation

Run No.	31	32	33
Polymerization Conditions			
Solvent	C - hex	C - hex	i - C ₈
Catalyst	2	2	2
Catalyst Concentration (Millimoles/Liter)	0.1	0.1	0.1
Al/V	12:1	12:1	12:1
Temperature, °C.	160	166	138
Time (Min.)	4	4	4
Pressure (psig)	120	120	104
Rotor Speed (rpm)	1100	0	0
Reaction Rate (Sec ⁻¹)	0.62	1.7	2.2
Phase Change Conditions			
Temperature, °C	—	—	121
Rotor Speed (rpm)	1100	0	1011
Shear Stress, (lb(f)/ft. ²)	—	0	—
($\delta_s - \delta_p$) ² cal/cc	—	—	3.67
Cooling Rate (°/min)	7.4	4.0	10.5
Polyethylene			
Yield (grams)	1.6	4.4	5.6
Description	2	3	2
Molecular weight $\times 10^{-6}$	1.09	1.12	2.78
Surface Area (m ² /g)	—	31.7	7.0
(η) dl/g	7.5	7.7	14.1
T _m °C	132	133	134

TABLE 10B (Continued)

Run No.	31	32	33
Handsheet Properties			
Tear Factor	74	29	50
Breaking Length (meters)	1899	1656	1703
Rupture Energy, ft.lbs./sq.ft.	7.8	4.8	14.9
Stretch (%)	13.8	8.2	21.8
Opacity, %	72	82	82
Scattering Coefficient, cm ² /g	262	421	455

Note: Runs 31—33 made in reactor of figure 2, cylindrical rotor.

EXAMPLE 14. Varying Catalyst and Polyethylene Concentration

The runs reported in Table 11 below illustrate that catalyst concentration has little effect on fibrous gel formation. Any catalyst concentration normally employed in the art may be employed in the present process. It is also seen that the concentration of polyethylene in the solution is almost directly proportional to the catalyst concentration, i.e., as catalyst concentration increases, the polyethylene concentration in the solution increases. Two runs (35P and 36P) were made with preformed polyethylene of high molecular weight for comparison to the other runs.

While in the foregoing Table 11 the polyolefin concentration in solution is shown to vary up to about 2% by weight, higher concentrations may be employed. The upper limit on polymer concentration is the solution is dictated by the necessity of forming a gel upon cooling and by viscosity considerations, i.e., a solution containing above about 15% by weight polyolefin becomes extremely viscous. Therefore, it is desirable to employ polyolefin concentrations less than about 15%, and preferably less than about 5% by weight. There does not appear to be any lower limit on polyolefin concentration.

Varying Catalyst and Polyethylene (PE) Concentration

TABLE II

Run No.	Polymerization Conditions										Phase Change Conditions							
	Solvent	Catalyst	Catalyst Concentration (Millimoles/Liter)	Al/V	Temperature, °C.	Time (Min.)	Pressure (psig)	Rotor Speed (rpm)	Reaction Rate (Sec ⁻¹)		Temperature, °C.	Rotor Speed (rpm)	Solution Viscosity, centipoises	Shear Stress, lb(f)/ft. ²	($\delta_s - \delta_p$) ² cal/cc	Cooling Rate (%/mm)	PE conc. (g/dl)	
34	C-hex	2	0.0004	12:1	138	4	100	1100	15.0		104	900	581	1.9	0.44	17.0	0.04	
35	C-hex	2	0.02	12:1	138	4	100	1200	9.9		110	500	733	1.3	0.5	13.4	0.13	
35 P	xy ^l										64	1000	—	—	0.09	0.9	0.3	
36	C-hex	2	0.1	12:1	138	4	100	200	7.2		109	200	2090	1.5	0.5	—	0.49	
36 P	xy ^l										92	950	—	—	0.02	1.0	1.0	
37	C-hex	2	0.5	12:1	138	4	100	90	5.0		113	70	3500	0.89	0.5	3.0	1.67	

TABLE II (Continued)

Run No.	Polyethylene									
	Yield (grams)	% Polymer (weight) in gel	Description	Molecular weight $\times 10^{-6}$	Surface Area (m^2/g)	(η) dl/g	T_m °C	% Crystallinity	Handsheet Properties	
									Tear Factor	Breaking Length (meters)
									Rupture Energy, ft.lbs./sq.ft.	Stretch (%)
									Opacity, %	Scattering Coefficient, cm^2/g
34	1.5	22.0	2	2.8	53.1	14	139	59	80	358
35	5.0	5.0	2	1.48	67.2	9.2	137	76	72	264
35 P	1.5	—	2	1.1	—	7.7	—	—	77	348
36	27.7	6.0	2	1.72	17.1	10.2	132	69	73	281
36 P	5.0	—	2	2.1	—	11.5	—	—	85	539
37	63.0	7.0	2	2.0	23.9	11.5	132	67	77	334

Note: Runs 34-37 made in reactor of figure 2, cylindrical rotor. Runs 35P & 36P were made with preformed polyethylene in the reactor of figure 1.

EXAMPLE 15.
Effect of Solubility Parameter
In the runs reported in Table 12 below, polymerization of ethylene or dissolution of preformed polyethylene was carried out in various solvents to illustrate the effect of solubility parameter upon fibrous gel formation and fiber properties. Runs 38, 40, 42 and 43 were polymerization runs and the other runs were dissolution runs wherein polyethylene was dissolved in the solvent at an elevated temperature. It is seen that in Run 47 wherein DMSO was the solvent that the solubility parameter thereof is too close to the outer limits of suitability, and only crumb was obtained instead of fibrous gel.

TABLE 12
Varying Solvent

Run No.	Polymerization or Solution Conditions	Solvent	Catalyst	Catalyst Concentration (Millimoles/Liter)	Al/Ti or Al/V	Temperature, °C.	Polyethylene Concentration (grams/ml) × 100 (%)	δ_g (25°C)	$(\delta_g - \delta_p)^2$ cal/cc	Reaction Rate (Sec ⁻¹)	Phase Change Conditions	Temperature, °C.	Rotor Speed (rpm)	Cooling Rate (%/min)
38		i-C ₈	2	0.1	12:1	139	1.0	6.85	3.16	8.3		93	1100	2.8
39		n-C ₈				109	1.0	7.55	1.4			96	900	1.0
40		Nujol	2	0.2	50:1	106	1.0	7.6	0.55	4.7		—	11300	6.7
41		n-C ₁₄				114	1.0	7.93	0.47			103	800	1.1
42		C-hex	2	0.1	12:1	138		8.18	0.18	6.7		118	1000	9.5
43		dec.	3	2.8	1.8:1	101		8.58	0.002	0.06		86	2000	7.1
44		xyl				94	1.0	8.84	0.03			93	740	1.1
45		tet				101	1.0	9.49	0.89			88	900	0.9
46		O-C ₆ H ₄ Cl ₂				101	1.0	10.04	1.5			85	660	0.7
47		DMSO				135	1.0	11.85	4.1			126.5	960	1.8

TABLE 12 (Continued)

Run No.	Polyethylene	Yield	% Polymer (weight) in gel	Description	Molecular weight $\times 10^{-4}$	Surface Area (m^2/g)	(η), dl/g	T _m , °C	% Crystallinity	Handsheet Properties	Tear Factor	Breaking Length (meters)	Rupture Energy, ft.-lb./sq.ft.	Opacity, %	Scattering Coefficient, cm^2/g
38	21	—	6.0	2	1.86	47.5	10.8	132	—	—	54.5	1739	32.5	92	800
39	—	—	6.0	2	0.49	41.3	4.4	125	61	—	40	1643	4.0	88	625
40	0.6	12.0	5.0	2	1.07	6.1	7.5	132	—	—	—	1516	2.2	87	510
41	—	5.0	6.0	2	0.23	3.9	2.7	120	74	—	100	1087	2.3	88	583
42	25.5	—	6.0	2	0.66	31.5	5.4	133	—	—	47	1988	6.8	74	264
43	4.7	5.0	5.0	2	0.69	7.1	5.5	137	—	—	50	487	0.4	96	998
44	—	5.0	—	2	0.44	24.5	4.1	125	—	—	41	1422	2.8	86	469
45	—	7.0	—	2	0.54	1.6	4.7	131	—	—	63	1757	4.8	85	487
46	—	3.0	—	2	1.47	4.3	9.2	131	—	—	56	1515	3.0	87	553
47	—	—	—	3	0.7	—	—	—	—	—	—	—	—	92	617

Note: Runs 38 and 42 made in reactor of figure 2, cylindrical rotor. Other runs (39, 40, 41 and 43—47) made in reactor of figure 1. Runs 38, 40, 42 and 43 were runs wherein ethylene was polymerized in the reactor. Other runs (39, 41 and 44—47) employed preformed polyethylene dissolved in the solvent at the temperature indicated.

EXAMPLE 16.
Higher Pressure Runs
The procedure and apparatus of example 11 was employed except that the polymerization of ethylene was carried out at a temperature 5 above the melt dissolution temperature. The results are reported in Table 13 below:

TABLE 13

Higher Pressure Polymerization

Run No.	Polymerization Conditions							
	Initial Pressure, atmospheres	Initial Temperature, °C.	VOCl ₃ (g. mmole/liter)	Reaction time (minutes)	Maximum temperature (°C)	Reaction rate (Sec ⁻¹)	Polyethylene	Yield (g)
	11.5	140	0.026	10	144	17.1	28.6	1,650
1	22	140	0.026	10	170	56.8	94.3	5,500
2	35	134	0.026	0.5	175	993	83	4,800
3	35	136	0.026	10	147	78.5	131.5	7,600
4	35	136	0.026	3	142	57.1	28.2	1,630
5	35	140	0.026	0.5	147	98.3	32.2	19,000
6	36	136	0.026	22	165	34.7	127.8	7,400
7	40	138	0.026	5	173	158	134.9	7,800
8								
Handsheet Properties								
	Breaking Length, meters	Tear Factor	Rupture Energy ergs/cm ² × 10 ⁻⁴	Scattering Coefficient*				
	1028	73.9	6.0	1500				
	1104	55	3.0	350				
	1404	—	8.9	876				
	796	43	2.0	180				
	1528	—	8.2	567				
	879	96	4.2	895				
	1264	117	2.8	240				
	1614	60	3.0	254				

*Average of two handsheets tested.

TABLE 14

PE Fibers (% by weight)	TAPPI Opacity, %	Basis Weight (pounds/3000 sq.ft.)	Caliper (Mils)
0	63.9	37.5	3.2
25	91.7	38.5	4.5
50	97.3	37.0	5.2
75	98.3	37.2	7.2
100	98.5	38.5	8.7

EXAMPLE 18.

Dye Receptivity

The polyolefin fibers of this invention have a remarkable ability to adsorb dye, in distinction to polyolefin staple which is not easily dyed. In this example, accurately weighed samples (0.1—0.5 grams) of various fibers were suspended in 50 ml. of water and well stirred while 100 ml. of a standard dye solution was added. The standard dye solution contains 0.01023 gram of Reactive Blue 86 per 100 ml. After stirring for three minutes, the mixture was made up to exactly 200 grams net weight with distilled water and filtered. The optical absorbance of the filtrate (D) is measured at 600 microns. A sample of the standard dye solution is diluted exactly 1:1

with water and its absorbance similarly measured (D_0). The optical density D of the sample filtrate and the dry weight W of the sample are used to calculate R, the dye receptivity, in grams of dye adsorbed per 100 grams of fiber sample by use of the following equation:

$$R = \frac{(D_0 - D) \times 0.01023 \times 100}{W \times 2 \times 0.40}$$

The results of testing the polyethylene fibers of this invention, polyethylene staple fibers (3 denier) and bleached kraft pulp (80 GR brightness) are reported in Table 15 below.

TABLE 15

Fiber Sample	D_0	D	W	R
PE Staple	0.32	0.31	0.50	0.03
Bleached Kraft	0.4	0.38	0.11	0.23
PE fibers of this invention*	0.4	0.2	0.11	1.8

*These fibers had a M_v of 1,500,000, a surface area of 49.8 m^2 /gram and a polyethylene density of 0.957 g/cc.

EXAMPLE 19.

Pigmented Fibers

This example illustrates that the fibers of the present invention may be pigmented. A high molecular weight linear polyethylene ($M_v = 600,000$) was dissolved in cyclohexane in the apparatus of figure 2 (cylindrical rotor operating at 1100 rpm) at 150°C. The cyclohexane contained a dry suspension (Englehard's Ultrawhite 90 kaolin coating clay). The total clay and polyethylene weight was 60 grams and 5.7 liters of cyclohexane was employed. The solution was slowly cooled to room

temperature with stirring, and a fibrous gel obtained. The fibrous gel was refined by two passes through a Sprout-Waldron disc refiner at 0.005 ml plate clearance. The resulting fibrous pulp was then solvent exchanged through isopropanol to water, and treated by the addition of 5% by weight (on the fibers) of starch to render the fibers water dispersible. Handsheets were made from the fibers in the standard manner. Ash content of the handsheets was measured to determine the clay loading level achieved. The results were as follows:

TABLE 16
Clay Loaded Sheets

Run No.	1	2	3
Nominal Clay, %	10	30	50
Actual Clay, %	6.7	17.2	21.3
Brightness, CE	90.3	90.5	89.7
Tappi Opacity	95.4	96.5	95.6
Scattering Coefficient	1325	1592	1366
Tensile	1.3	1.4	1.0
Rupture Energy	0.4	0.4	0.2
Tear Factor	59.7	34.4	30.4

The fibers produced by the process of the present invention may be employed for those uses to which fibers are normally employed. The principal utility is in the areas of forming non-woven webs and in textile applications by spinning yarn from the fibers. Other uses include molding, insulation, coatings, laminate reinforcement and filter manufacture.

The words "Whatman", "Teflon" and "Nujol" used in this specification are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. A process of preparing polyolefin fibres which comprises firstly forming a gel of high molecular weight linear polyolefin, said gel comprising a fibrillar structure of fibrous polyolefin defining a network of interconnecting capillary spaces filled with organic solvent, any shear stress applied in formation of the gel being insufficient to form discrete polyolefin fibres, and secondly subjecting the gel to a shear stress sufficient to form discrete polyolefin fibres.
2. A process according to claim 1 in which in the first step there is formed a gel containing microfibrils and containing also macrofibrils having a diameter greater than 1 micron and up to 20 microns.
3. A process according to claim 2 in which in the second step there are formed discrete polyolefin fibres having dimensions of the same order of magnitude as cellulosic paper-making fibres.
4. A process according to claim 1, in which the gel is formed by polymerizing an olefin in the presence of a coordination catalyst and in a solvent for the polymer, at a temperature below the melt dissolution temperature of the resultant polymer in the solvent and at a sufficiently rapid reaction rate to effect formation of the gel.
5. A process according to claim 4 and claim 2 or 3, in which a shear stress is applied to the polymerization mixture sufficient to ensure the presence of macrofibrils in the gel, but insufficient to cause the presence of discrete fibres.
6. A process according to claim 1, in which the gel is formed by polymerizing an olefin in the presence of a coordination catalyst and in a solvent for the polymer, at a temperature above the melt dissolution temperature of the polymer, and then cooling the resultant solution.
7. A process according to claim 6 in which the solution is formed at a temperature below the temperature of molecular randomization (as herein defined).
8. A process according to claim 7 and claim 2 or 3, in which the polymer solution is subjected during cooling to a shear stress sufficient to ensure the presence of macrofibrils in the gel, but insufficient to cause the presence of discrete fibres.
9. A process according to claim 6 and claim 2 or 3, in which the polymerization is effected at a temperature above the temperature of molecular randomization (as herein defined), and is subjected during cooling to a shear stress.
10. A process according to claim 2 or 3, in which the gel is formed by dissolving olefin polymer in a solvent therefor, and cooling the resultant solution while subjecting the solution

to a shear stress sufficient to ensure the presence of macrofibrils in the gel but insufficient to cause the presence of discrete fibers.

11. A process according to any preceding claim in which the polyolefin is polyethylene or polypropylene having a viscosity average molecular weight greater than 500,000.

12. A process according to any preceding claim in which the polyolefin has a viscosity average molecular weight greater than 1,000,000.

13. A process according to claim 4 or 6 in which the polymerization is effected in the absence of a chain transfer agent.

14. A process according to any of claims 4 to 9, in which the olefin monomer is gaseous and the reaction medium is saturated with the olefin monomer prior to introduction of the catalyst.

15. A process according to any of claims 4 to 9 together with claim 11 or 12, in which the solubility parameter of the reaction solvent

is between 6.0 and 10.0 (cal/cc)^{1/2}.

16. A process according to claim 15, in which the reaction medium is cyclohexane, decalin, heptane, tetralin, *m*, *o* or *p*-xylene, a chlorinated hydrocarbon solvent, toluene, hexane, isooctane, a mineral oil, n-octane, p-cymene or a mixture thereof.

17. A process according to any preceding claim, in which the formation of discrete polyolefin fibers from the gel is effected by passing the gel through a disc refiner.

18. A process according to claim 1, substantially as hereinbefore described.

19. Polyolefin fibers prepared by a process according to any preceding claim.

20. A non-woven web comprising fibers according to claim 19.

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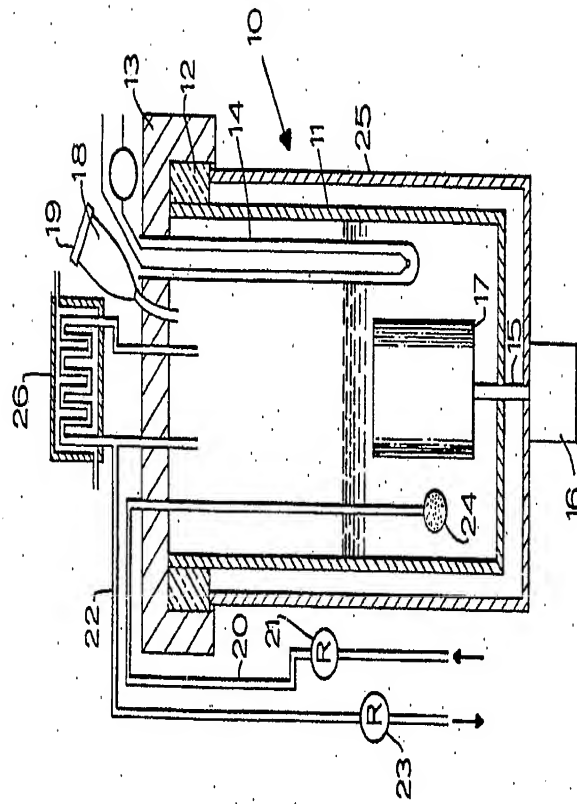
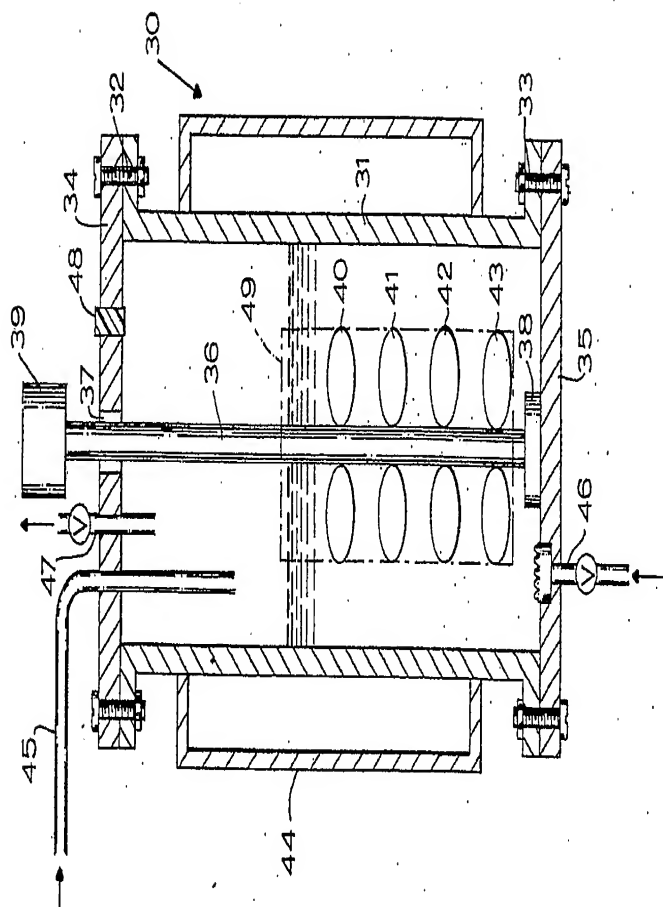


FIG. 1



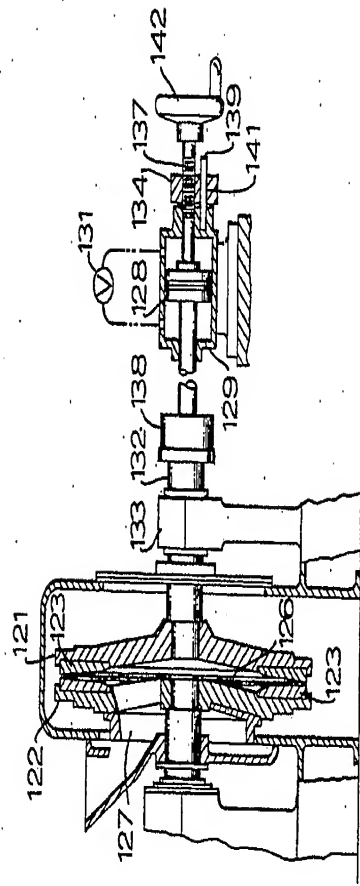


FIG. 3

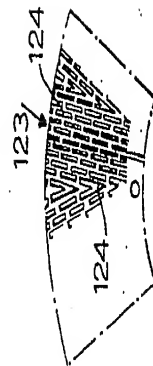


FIG. 4

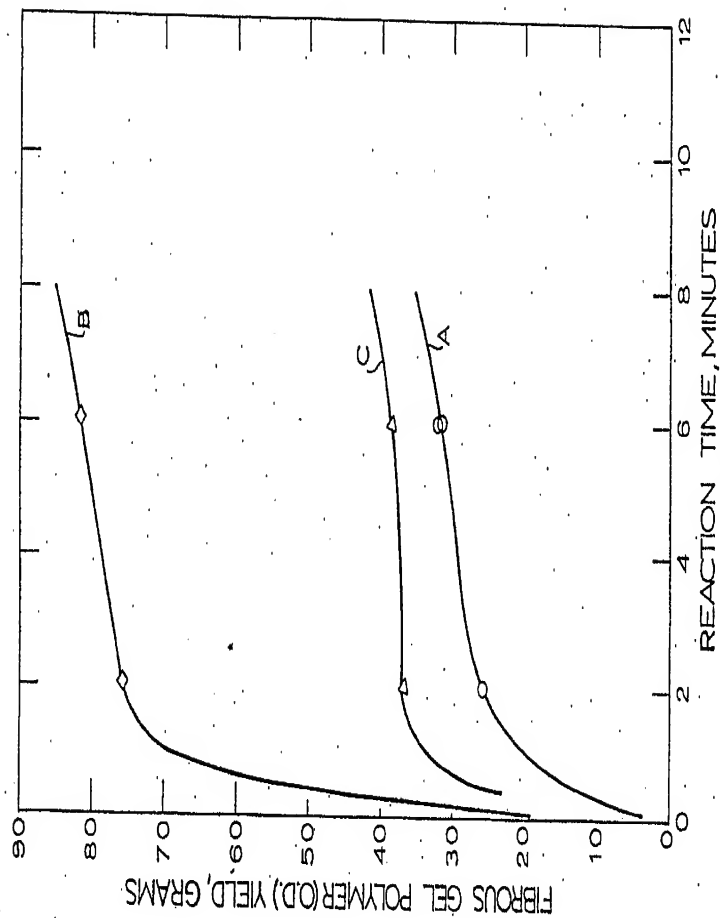
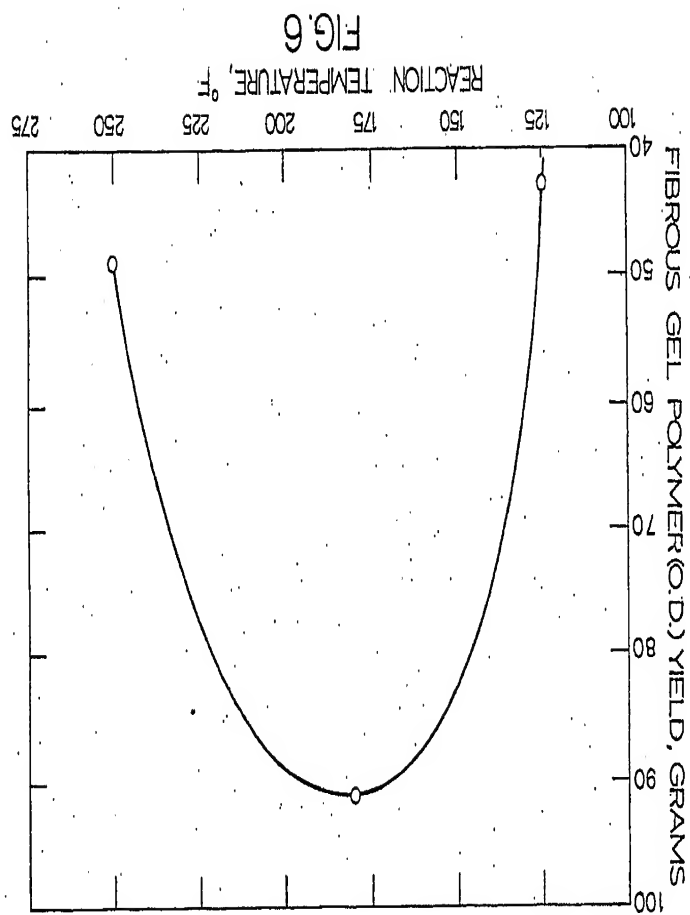


FIG. 5



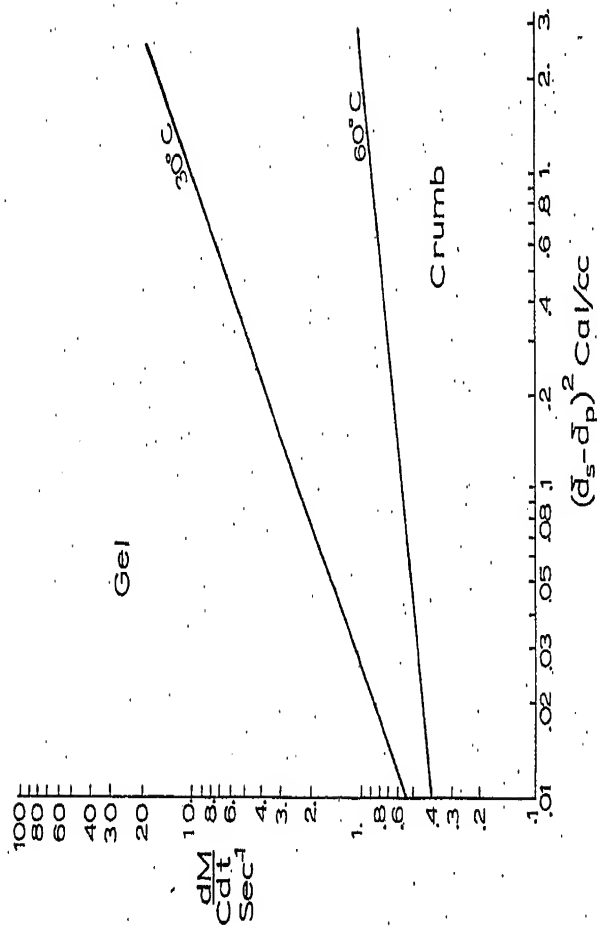


FIG. 7



FIG. 8

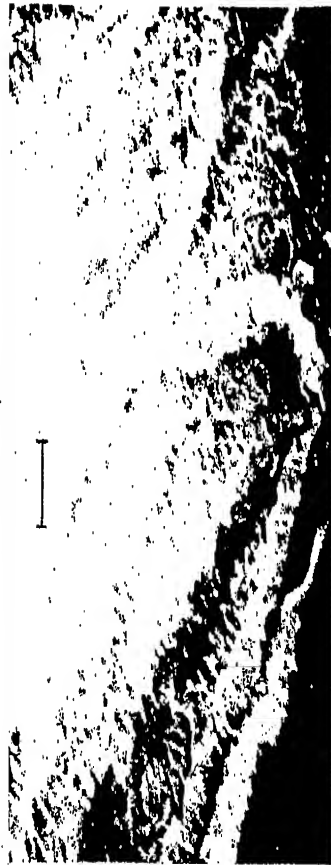


FIG. 9